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Avogadro and Dalton

The Standing in Chemistry of their Hypotheses

BY

ANDREW N. MELDRUM, D.Sc.

WITH A PREFACE BY

FRANCIS R. JAPP, M.A., LL.D., F.R.S.

Professor of Chemistry in the University
of Aberdeen

Aberdeen
Printed for the University
1904

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Avogadro and Dalton

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PREFACE.

The important question whether, in discussing the constitution of matter, the atom or the molecule should be first considered, is one regarding which there has been considerable difference of opinion among chemists.

Formerly, few would have disputed the claim of the atom to prior consideration. Not only did Dalton's atomic hypothesis precede Avogadro's molecular hypothesis in order of time, but this chronological order seemed also to be the natural order, involving, as it did, only the usual transition from the simpler to the more complex conception.

But the history of the science shows that, enormous as were the services which Dalton's atomic hypothesis rendered to chemistry, the chief object of that hypothesis—the determination of a set of consistent atomic weights—remained for a long time merely a pious hope. Avogadro's rule supplied a means of determining the molecular weights of substances, and, from these molecular weights, of ascertaining which of several possible atomic weights of a contained element was the correct one. Until this step had been taken, the marvellous developments of theoretical chemistry which have characterised the last fifty years would have been impossible.

In the study of the constitution of matter, therefore, we are compelled, by the very nature of the particular problems of scientific measurement and calculation involved, to reverse what is apparently the natural order of things and to proceed from the more complex to the simpler—from highly complex objects of sense to successively simpler and simpler conceptual structures underlying these. Thus the order of quantitative determination is :—(1) relative weights of comparable amounts of *matter in bulk* (gaseous or dissolved); (2) relative weights of *molecules;* (3) relative weights of *atoms;* and (4), if subsequent experiment should justify the most recent speculations, mass of *electrons.*

The view here stated as to the true ratiocinative order of precedence of the molecular and atomic hypotheses has been held by various chemists; but I have nowhere else seen it expounded with such wealth of illustration and with so exhaustive a knowledge of the fundamental literature of the subject, as in the present monograph by Dr. Meldrum.

FRANCIS R. JAPP.

UNIVERSITY OF ABERDEEN,
30th September, 1904.

AUTHOR'S PREFACE.

Some of the books required for the purposes of this essay were purchased by means of a grant from the Carnegie Trustees. The publication of the essay has been made possible by another grant from the same body.

I am indebted to Mr. Joseph Knox, B.Sc., who went over the essay in a friendly, critical way, and canvassed difficulties with me till a solution was reached.

— ANDREW N. MELDRUM.

UNIVERSITY OF ABERDEEN, 1904.

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ABBREVIATIONS.

A. C. R.,	Alembic Club Reprints.
Chemical Philosophy,	Tilden's Chemical Philosophy, 1901.
Cooke,	Cooke's New Chemistry, 1874.
C. N.,	Chemical News.
Delamétherie,	Delamétherie's Journal de Physique.
Divers,	British Association, 1902, Section B, President's Address, Separate Reprint.
E. B.,	Encyclopædia Britannica, 9th Ed.
Essai, 1819,	Berzelius' Essai sur la Théorie des Proportions Chimiques, 1819.
Essai, 1835,	Berzelius' Essai sur la Théorie des Proportions Chimiques, 1835.
Gmelin,	Gmelin's Handbook of Chemistry, Watt's Translation.
Heat,	Clerk Maxwell's Theory of Heat, 10th Ed.
Henry,	Henry's Memoirs of Dalton, 1854.
J. C. S.,	Journal of the Chemical Society of London.
Klassiker,	Ostwald's Klassiker.
Ladenburg,	Ladenburg's History of the Development of Chemistry, Dobbin's Translation, 1900.
Von Meyer,	Ernst von Meyer's History of Chemistry, McGowan's Translation, 1898.
Morley,	Smithsonian Contributions to Knowledge, 980, The Densities of Oxygen and Hydrogen, Morley.
Nernst,	Nernst's Theoretical Chemistry, Palmer's Translation, 1895.
Ostwald,	Ostwald's Principles of Inorganic Chemistry, Findlay's Translation, 1902.
Roscoe,	Roscoe's John Dalton and the Rise of Modern Chemistry, 1895.
Short History,	Tilden's Short History of the Progress of Scientific Chemistry, 1899.
Thorpe,	Essays in Historical Chemistry, 1902.
Traité,	Gerhardt's Traité de Chimie Organique.
Zeitschrift,	Zeitschrift für Physikalische Chemie.

PART I.

The Standing in Chemistry of Avogadro's Hypothesis.

CHAPTER I.

INTRODUCTION.

Truth on these subjects is militant and can only establish itself by means of conflict.—J. S. MILL.

At the outset of this essay, it is well to state an axiom which is much used in the course of the argument. It is assumed that there is an essential distinction between what are known on the one hand as laws and on the other hand as hypotheses. A hypothesis is the creation of the mind, and is of service in interpreting a law. There is good ground for the belief that in science the recognition of this distinction between law and hypothesis is an indispensable condition of clear thinking.

The distinction has been insisted on by Faraday. His words are:—"It is always safe and philosophic to distinguish, as much as is in our power, fact from theory; the experience of past ages is sufficient to show us the wisdom of such a course; and considering the constant tendency of the mind to rest on an assumption, and, when it answers every present purpose, to forget that it is an assumption, we ought to remember that it, in such cases, becomes a prejudice, and inevitably interferes, more or less, with a clear-sighted judgment. I cannot doubt but that he who, as a wise philosopher, has most power of penetrating the secrets of nature, and guessing by hypothesis at her mode of working, will also be most careful, for his own safe progress and that of others, to distinguish that knowledge which consists of assumption, by which I mean theory and hypothesis, from that which is the knowledge of facts and laws; never raising the former to the dignity or authority of the latter, nor confusing the latter more than is inevitable with the former."[1]

Very recently Richards, his views on a question of the day having been much misunderstood, had occasion to emphasise the distinction. He refers to a question the discussion of which, "as of so many scientific questions, has been much confused by the inability of many writers to distinguish between fact and hypothesis. . . . Facts are determined by observation and experiment, and their truth depends only upon the accuracy of the observation and experiment. Their discovery is a lasting addition to the knowledge of mankind. On the other hand, hypotheses are attempts to interpret the facts; and many hypotheses, from their very nature, can never be proved."[2]

Obvious as this distinction may seem, it is necessary to lay emphasis on it here, in view of the persistence with which certain chemists use the term Avogadro's law, instead of Avogadro's hypothesis. In this essay, Avogadro's hypothesis is regarded as an interpretation put upon Gay-Lussac's law. The law, unlike the hypothesis, is matter of fact, and must remain so, even should the hypotheses which are made to explain it be multiplied.

Science is coming more and more into use in education. So used, one of the benefits of science is understood to be that it inculcates logical ways of thinking.

"What a retrospect," says Gibbon, "is it to a genius truly philosophical . . . to find true consequences falsely deduced from the most erroneous principles." As a training in thinking, the study of experimental science presents one risk: logic is one thing, and experiment is another. The chemist habitually examines how far his conclusions square with the facts, and as to the facts, need not go very far wrong. Nevertheless, "true consequences may be falsely deduced from the most erroneous principles." The conclusions squaring with the facts, it does not follow that the logic which yields the conclusions is sound.

---

[1] Experimental Researches in Electricity, vol. II., 1844, p. 285.

[2] C.N., 88, 69.

To show that the logic of chemistry is not always sound, it is sufficient to consider the treatment, in many of the books on chemistry, of the subjects of molecular-weight and atomic-weight determination. The connection between the several molecular-weight methods and the definition of the molecule is left in obscurity. How different is the treatment in physics of the subject of specific-gravity, for instance! Specific-gravity having been defined, some effort is made to show that the several specific-gravity methods are in accordance with the definition. On the other hand, the molecular-weight methods are stated in such a way as to leave on the student's mind the impression that each of these methods stands on its own footing, and is independent of the definition of the molecule. The treatment of the subject of atomic-weight methods is similar; the books give the impression that the different atomic-weight methods have no connection that can be shown with one another, or with the definition of atomic-weight, and that they yield concordant results for all that.

The "Theoretical Chemistry" of Nernst is written, as the title-page states, "from the standpoint of Avogadro's Rule and Thermodynamics." The subject of Thermodynamics may be regarded as non-hypothetical, since it consists essentially of a development by the aid of mathematics and dynamics of the two fundamental laws of Thermodynamics, and makes no assumption as to the continuity or discontinuity of matter. The theoretical basis of Nernst's system of chemistry is Avogadro's hypothesis.

Nernst's book is a comprehensive one, suitable for the student of research. It goes as far as the debatable ground between the known and the unknown. It was doubtless foreign to Nernst's purpose to expatiate on the rudiments of chemistry. There is reason to believe that it would be of interest, and even of value, to trace the development, in logical order, of the cardinal doctrines of chemistry on the basis of Avogadro's hypothesis.

The standing of Avogadro's hypothesis in chemistry is still an open question. Strange as this may seem, it can easily be made manifest by reference to the literature of chemistry. For instance, I quote the verdicts on this question of Cooke and Divers.

Cooke states that in writing "The New Chemistry" he made it his object "to present the modern theories of chemistry," and "to give to the philosophy of the science a logical consistency, by resting it on the law of Avogadro."[1]

Divers, as President of the Chemical Section of the British Association in 1902, took a very different view from Cooke. The credit given to Avogadro by Cooke, is given by Divers to Dalton. In the Presidential Address, Divers had occasion "to restate and examine most of the fundamental and familiar principles of our science."[2] Accordingly, Divers expounds "the theory of chemistry, which, with all its modern developments, I take to be indisputably the theory of Dalton."[3] Again, "the theory of chemical molecules was brought to light . . . not by Avogadro's hypothesis," he says, "but in the first place by Dalton's atomic theory and Gay-Lussac's law . . . ; and then, much more fully in the middle of the last century, through the brilliant work of Gerhardt, Williamson, Laurent, Odling, Wurtz, and others, in the purely chemical field."[4] Apparently, in Divers' judgment, the historical importance of Avogadro's hypothesis is slight.

Not only so, but speaking of the same hypothesis, Divers says, "unfortunately it does not hold good in the case of not a few simple substances."[5]

True, chemical theory did not stand still in the interval between 1873, when Cooke was writing, and 1902, the date of Divers' address. There was in the interval development and expansion of the old ideas; but nobody maintains that there has been, since 1870, a revolution in chemical ideas. It is impossible to maintain that this contradiction between Cooke and Divers is significant of some change, amounting to an upheaval, in chemical theory.

If a sound method for the advancement of a science consists in "constant recurrence to first principles," in what a position of difficulty and embarrassment are the devotees of chemistry placed. In regard to first principles, here are the high-priests of chemistry giving decisions which, to use plain language, are in flat contradiction to one another.

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[1] Cooke, p. 5. [2] Divers, p. 2. [3] Loc. cit., p. 3. [4] Loc. cit., p. 8. [5] Loc. cit., p. 12.

Controversy is not always a bad thing. Subjects there are on which " truth is militant, and can only establish itself by means of conflict." Surely chemists would do well to make up their minds about first principles, and to make their reasons known, even at the risk of raising controversy.

No further explanation can be given for the attempt in the following essay to consider the questions of the standing in chemistry first of Avogadro's hypothesis, and afterwards of Dalton's atomic theory. Reasons will be given later for taking the questions in this order.

Avogadro's hypothesis is the subject of the first part of this essay. After consideration of the hypothesis as such, it is taken as a starting-point, from which to develop, as logically as may be, the ideas such as molecular-weight, atomic-weight, valency, radicals, etc., which are second nature to the chemist.

CHAPTER II.

THE RELATION OF THE HYPOTHESIS TO GAY-LUSSAC'S LAW.

Since all progress of mind consists for the most part in differentiation, in the resolution of an obscure and complex object into its component aspects, it is surely the stupidest of losses to confuse things which right reason has put asunder.—PATER.

Gay-Lussac's "Memoir on the Combination of Gaseous Substances with each other" was read in 1808 and issued in print in 1809. The subject of this paper is what is known as Gay-Lussac's law. The law is: "Not only do gases combine in very simple proportions" by volume, "but the apparent contraction of volume which they experience on combination has also a simple relation to the volume of the gases, or at least to that of one of them."[1]

Rich in experimental discoveries, Gay-Lussac's memoir is comparatively destitute of speculations and hypotheses. Berzelius remarks on this: "M. Gay-Lussac was satisfied with having determined the ratios in which gaseous substances combine, but he made no wider application of this discovery."[2]

In 1811, on consideration of this law, Avogadro published his hypothesis, namely, "That the number of (integral) molecules in any gases is always the same for equal volumes, or always proportional to the volumes."[3]

It is surprising that Gay-Lussac did not himself anticipate Avogadro. The reason why can only be guessed at. With some men of science, with Dalton, for instance, the faculty of speculation is predominant; with others, with Bunsen, for instance, the ruling passion is the making of experiments. It may be that Gay-Lussac resembled Bunsen. But whatever the explanation, a division of labour there was between Gay-Lussac and Avogadro. Stronger witness there could hardly be to the distinction between law and hypothesis, than the enunciation of a law in 1808 by Gay-Lussac, and the enunciation of a hypothesis, by way of explanation of the law, in 1811 by Avogadro.[1]

---

[1] A.C.R., 4, 15.

[2] "M. Gay-Lussac se contenta d'avoir démontré les rapports dans lesquels se combinent les substances gazéiformes, ... mais il ne fit point d'application plus générale de cette découverte."—Essai, 1819, p. 14.

[3] A.C.R., 4, 29.

Plain as is the above distinction between Gay-Lussac's teaching and Avogadro's, all the more surprising is the amount of established error on the subject in the books, and the extent to which the distinction has been ignored by men of science. Error has arisen in three several ways.

In the first place, the assertion is made that the object of Avogadro's hypothesis was other than the interpretation of Gay-Lussac's law. One of the traditions of chemistry is that Avogadro formed his hypothesis on contemplation of the physical properties of gases and as an interpretation of these properties. Among the authorities who maintain and diffuse this tradition is the great Encyclopædia Britannica. "In 1811, Avogadro, remarking that equal variations of temperature and pressure produce in all gases and vapours the same change of volume, enunciated the hypothesis that equal volumes of any gas or vapour contain the same number of atoms."[2]

According to this account of the genesis of the hypothesis, the physical properties of gases, *i.e.*, Boyle's law and Charles' law, formed the main consideration with Avogadro, so that Gay-Lussac's law was at most a minor consideration, if it was considered at all. This account is in no way confirmed by a scrutiny of Avogadro's paper; the contrary is evidently the case, that what suggested the hypothesis to Avogadro was Gay-Lussac's law. What Avogadro had in view when he formulated his hypothesis, what he refers to at the outset of his paper and takes into consideration throughout, is Gay-Lussac's law.

This erroneous account was corrected by Ostwald in 1889.[3] Nevertheless Ladenburg, in a book published in 1900, persists in the error. "The physical properties of the gases (especially the similarity in their behaviour towards changes of pressure and of temperature) lead Avogadro to assume in equal volumes of all gases, the same number of molecules."[1]

---

[1] The statement, that Avogadro's hypothesis is an explanation of the properties of gases, does not mean that Avogadro explained why one gas combines with another. There is little need to emphasise this, so far as the main purpose of this essay is concerned, because chemical affinity was explained just as little by Dalton as by Avogadro.

[2] E. B., Article Chemistry—Historical Introduction by F.H.B.

[3] Klassiker, 8, 48.

The matter can be put beyond doubt by quoting Avogadro's own statement, in his second paper on the subject. "In my essay on 'A Method of Determining the Relative Masses of the Molecules of Substances, etc.,' I have advanced a hypothesis . . . in order to explain the fact discovered by M. Gay-Lussac, that the volumes of the gaseous substances which combine with one another, and of the compound gases which are produced, are always in simple ratios to one another."[2]

In the second place, Gay-Lussac's law and Avogadro's hypothesis have been regarded as the same thing. Clerk Maxwell mentions "a very important law established by Gay-Lussac, that the densities of gases are proportional to their molecular weights."[3] The statement which Clerk Maxwell here describes as Gay-Lussac's law is familiar to chemists as the equivalent of Avogadro's hypothesis.

Nevertheless, Gay-Lussac's law and Avogadro's hypothesis are not the same thing. The two generalisations are distinct, no matter how natural the step from the law to the hypothesis may seem, and no matter how obvious a corollary of the hypothesis the law may be. On this point the history of the subject affords a decisive verdict. The two generalisations were enunciated at different times by different men. Again, while the law came at once into almost, if not quite, universal acceptance with chemists, the hypothesis for long met with neglect, or was revived only to be rejected. Revived, and applied successfully at last to organic chemistry by Gerhardt and Laurent, the hypothesis was accepted without reserve, and applied successfully to both organic and inorganic chemistry, first by Cannizzaro about the year 1858.

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[1] Ladenburg, p. 61.

[2] "Dans mon *Essai d' une Manière de déterminer les Masses relatives des Molécules des corps, etc.*, j'ai proposé une hypothèse pour expliquer le fait découvert par M. Gay-Lussac, que les volumes des substances gazeuses qui se combinent entre elles, et des gaz composés qui en résultent, sont toujours dans des rapports très simples entre eux." Delamétherie, 1814, 78, 131. The reference to the first paper is Delamétherie, 1811, 78, 58

[3] Heat, p. 326.

In the third place, Avogadro's hypothesis is frequently described as a law. Tilden, for instance, under the heading, "the law of Avogadro," remarks, "This statement, originally enunciated by an Italian physicist, Avogadro, . . . may now be regarded as a well-established truth."[1]

This is not a mere matter of words. The point lies in the statement that this particular doctrine, whether it be called Avogadro's hypothesis or Avogadro's law, is "now a well-established truth." It is one of the tenets of this essay that the doctrine, far from being a "well-established *truth*," is, on the contrary, one of the hypotheses, which, from their very nature, have never been proved.

Avogadro himself, presumably, regarded the doctrine as an assumption; he uses the term "hypothesis." To use the term "law" is only to give way to what Faraday calls "the constant tendency of the mind to rest on an assumption, and, when it answers every present purpose, to forget that it is an assumption."

The use of the term "law" in this connection has two results. First, it tends to keep the hypotheses which form the basis of nineteenth century science out of sight. Second, and this will be considered in the next chapter, it is likely to conceal the truth that hypotheses are of a transient nature.

About the constitution of matter, there are, according to Clerk Maxwell, "two modes of thinking, which have had their adherents both in ancient and in modern times. They correspond to the two methods of regarding quantity—the arithmetical and the geometrical. To the atomist the true method of estimating the quantity of matter in a body is to count the atoms in it. The void spaces between the atoms count for nothing. To those who identify matter with extension, the volume of space occupied by a body is the only measure of the quantity of matter in it."[2]

From this point of view it is of much interest to consider the measurement of matter in chemistry. The method is, to measure matter in the gaseous state, by taking equal volumes of the different gases. At the present time, the use of this method pure and simple is being inculcated by Ostwald. Chemistry, as expounded by him, is a science which "identifies matter with extension."

---

[1] Chemical Philosophy, p. 16.

[2] E. B., Article Atom.

On the contrary, as understood by the chemists of the school of Dalton and of Avogadro, chemistry is a science of molecules and atoms. Yet, so far as results go, there is no difference between the opposing schools; they both measure matter in the same way, by taking equal volumes of different gases. This, according to Avogadro, is a means of taking equal numbers of the different molecules. Ostwald, on the other hand, simply refrains from postulating the existence of molecules.

The accepting of Avogadro's hypothesis as a law lies open to the objection that the hypothesis assumes the discontinuity of matter. As Clerk Maxwell has stated, "there are two ways of thinking about the constitution of bodies, which have had their adherents both in ancient and in modern times." Avogadro's hypothesis is not a law, because it implies the adoption of the atomistic way of thinking about matter, and the rejection of the other way.

The trend of nineteenth century science, obviously, has not been such as to train and brace the mind for the conception of continuous matter. It is sometimes said that a theory of continuous matter is "inconceivable." Those who say so may be supposed to know their own minds best. There is, nevertheless, the possibility that the theory of the future may not regard matter as atomic. Ostwald, in the theory which he is at present formulating, makes no assumption as to the constitution of matter.

Whatever the event, it is certain that some leaders of science have been agnostics in regard to the atomic theory. Of these Faraday was one, and Frankland another. In 1869, in the course of a discussion at the Chemical Society of London on the atomic theory, Frankland said he was "averse to accepting the theory as an absolute truth." "He considered it impossible to get at the truth as to whether matter was composed of small and indivisible particles, or whether it was continuous—the question belonged to what the metaphysicians termed 'the unknowable'; but he acknowledged the importance of the fullest use of the theory as a kind of ladder to assist the chemist in progressing from one position to another in his science." "He did not wish to be considered a blind believer in the theory, or as unwilling to renounce it if anything better presented itself to assist him in his work."[1]

In 1853, Faraday, invited to express his opinions on the atomic theory, for publication in Henry's "Life of Dalton," wrote—"*I believe in matter and its atoms* as freely as most people, at least I think so. As to the little solid particles which are by some supposed to exist independent of the forces of matter . . . as I cannot form any idea of them apart from the forces, so I neither admit nor deny them. They do not afford me the least help in my endeavour to form an idea of a particle of matter. On the contrary, they greatly embarrass me . . . the notion of a solid nucleus without properties is a natural figure or stepping-stone to the mind at its first entrance on the consideration of natural phenomena; but when it has become instructed, . . . the notion becomes to me hypothetical, and what is more, a very clumsy hypothesis."[2]

---

[1] J. C. S., 22, 435. [2] Henry, p. 132.

CHAPTER III.

THE RELATION BETWEEN THE HYPOTHESIS AND THE KINETIC THEORY OF GASES.

> *Generally, let this be a rule, that all partitions of knowledges be accepted rather for lines and veins than for sections and separations; and that the continuance and entireness of knowledge be preserved. For the contrary hereof hath made particular sciences to become barren, shallow, and erroneous, while they have not been nourished and maintained from the common fountain.*—BACON.

The term molecule is used both in chemistry and physics. The physical molecule, as defined by Clerk Maxwell, is "that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas."[1] The question is sometimes considered, is the physical molecule the same thing as the chemical molecule?

One answer that may be given is, that the two ideas, though they have different phenomena in view, are not incompatible with one another. The physical molecule can doubtless, on occasion, take part in chemical action. The chemical molecule, while its chemical activity is in abeyance, doubtless "moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas." This is important, because it means the possibility of a molecular theory which shall bring both chemical and physical phenomena into co-ordination with one another. Thus a collision between two molecules must occur, as one condition that chemical action shall take place between them.

Divers, in his British Association address in 1902, opposes any identification of the chemical with the physical molecule. . . . "the atomic theory should be called the molecular theory of chemistry, . . . were it not for fear of confounding it with the mechanical theory of that name."[2]

What Divers understands by the atomic theory he has explained in the most explicit manner. "Divested of all reference to the physical constitution of matter, the atomic theory is that the quantities of substances which interact in single chemical changes are equal to one another—as truly equal in one way as equal masses are in another—and, therefore, that chemical interaction is a measure of quantity of unlike substances, distinct from and independent of dynamical or mass measurement."[1]

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[1] E. B., Article Atom. [2] Divers, p. 4.

Divers admits that "Dalton, indeed, did not express himself in any such terms, his mind being fully possessed with the ancient and current belief upon which he framed his theory that substances are made up of minute discrete particles. But it is clear enough that his theory was that of the existence of another order of equality between substances than that of weight."[2] Accordingly, Divers formulates an atomic theory which is "divested of all reference to the physical constitution of matter."

It is no easy matter to do justice to a version of Dalton's atomic theory so out of the ordinary as this. What I understand Divers to maintain is, that, in addition to the two ways, recognised by Clerk Maxwell, of thinking about matter, there is a third way, of which chemists are the exponents. In case the conclusion of this essay is just, namely, that in chemical theory Avogadro's hypothesis is the "controlling and organising pri[illegible]e," this third way of thinking about [illegible]er is fallacio[illegible]

In any [illegible] phraseology of this third way, as fixed by [illegible]vers, is [illegible]ly to lead to confusion. The words "atom" [illegible] "[illegible]" are [illegible]acteristic of one of the two ways of [illegible]ki[illegible] about [illegible] t [illegible]gnised by Clerk Maxwell, and they [illegible]h it fr[illegible] the ot[illegible] way. The words "atom" and [illegible]" [illegible] d[illegible] by Divers in connection with his [illegible]y of thinki[illegible] about [illegible]ter, the result is, that he makes [illegible] of the [illegible] wo[illegible] as Clerk Maxwell as a means of [illegible]nveying totally dif[illegible] ideas. Since the words "atom" [illegible] "molecule" were used by Dalton with reference to the [illegible]cal constitution of matter, surely, in the eyes of the [illegible]rs of Dalton, one is justified in continuing to use them [illegible] in this sense.

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[1] Loc. cit., pp. 3-4. [2] Loc. cit., p. 4.

> *The function of physical science is seen to be much more modest than was at one time supposed. We no longer hope by levers and screws to pluck out the heart of the mystery of the universe. But there are compensations. The conception of the physical world as a mechanism, constructed on a rigid mathematical plan, whose most intimate details might possibly some day be guessed, was, I think, somewhat depressing. We have been led to recognise that the formal and mathematical element is of our own introduction; that it is merely the apparatus by which we map out our knowledge, and has no more objective reality than circles of latitude and longitude on the sun. . . . . The world remains a more wonderful place than ever; we may be sure that it abounds in riches not yet dreamed of.*—HORACE LAMB.

Not only is it objectionable to call Avogadro's hypothesis a "law," since Avogadro used the term "hypothesis," but also because it is likely to keep the hypotheses which form the basis of nineteenth century science out of sight. This has been shown in Chapter II. There is another objection, which will now be considered, that it tends to conceal the truth that hypotheses are of a transient nature.

Avogadro's hypothesis is found to be a deduction from the kinetic theory of gases. Primarily, this theory contemplates the physical properties of gases. It makes certain assumptions as to the nature of gaseous matter, from which, by mathematical and dynamical reasoning, Boyle's law, Charles' law, Avogadro's hypothesis and Gay-Lussac's law can be deduced. It is on this account, doubtless, that many scientific writers have come to regard Avogadro's hypothesis as being on precisely the same footing as Boyle's, Charles', and Gay-Lussac's laws. It is accordingly described by these writers as a law.

This is a specious reason for calling Avogadro's hypothesis a law. A deduction from a theory must stand or fall with the theory. What then are the fundamental assumptions of the kinetic theory of gases? They are:—

1. That matter is composed of a finite number of molecules. In a gas the volume of a single molecule is small compared with the space which the molecule is occupying.

2. That the molecules are in perpetual motion from place to place, the motion of single molecules being disturbed by collisions with other molecules and with the containing wall.

3. That on collision, there is no change of energy of

translation into energy of rotation. Hence it is necessary to picture the molecule as a smooth hard sphere.

4. That the condition of dynamic equilibrium between two sets of molecules of different kinds (*i.e.*, $M_1c_1^2 = M_2c_2^2$, M denoting mass and c velocity), is also the condition of thermal equilibrium.

On the four assumptions of the kinetic theory of gases, it can be shown by dynamics that when p denotes the pressure of a gas, and N the number of molecules in unit volume of the gas, $3p = MNc^2$.

For two different gases, $3p_1 = M_1N_1c_1^2$, and $3p_2 = M_2N_2c_2^2$
If the pressures be equal, $M_1N_1c_1^2 = M_2N_2c_2^2$
If the temperatures be equal, $M_1c_1^2 = M_2c_2^2$
Hence $N_1 = N_2$
and this is Avogadro's hypothesis.

The accepting of Avogadro's hypothesis as a law, on the strength of the kinetic theory of gases, is open to objection, because the kinetic theory of gases itself is not above suspicion. In reference to the current view of the molecule, Tait says, "the hard atom . . . survives to this day . . . as at least an unrefuted, though a very improbable hypothesis."[1] The successive changes, from the emission theory of light to the undulatory theory, and from the undulatory theory to the electro-magnetic theory, were made in order to embrace a wider and wider range of phenomena.[2] The kinetic theory ignores the problems of gravitation and chemical affinity, and therefore can hardly be final. Were the kinetic theory abandoned, in favour of a theory which does explain gravitation and chemical affinity, then the laws of Boyle, Charles, and Gay-Lussac must be deductions from the new theory, but who can say in advance that the theory will lead to Avogadro's hypothesis?

Scrutiny of the fundamental assumptions of the kinetic theory of gases shows that one of them lies open to particular objection. This is the doctrine, namely, that two sets of molecules in dynamical equilibrium are also in thermal equilibrium. By Clerk Maxwell this doctrine has been expressly recognised to be a pure assumption.

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[1] Properties of Matter, 4th ed., p. 18.

[2] This illustration of the transient nature of scientific theories is taken from Ostwald's "Emancipation from Scientific Materialism."

He says, "If the system is a gas or mixture of gases not acted on by external forces, the theorem that the average kinetic energy for a single molecule is the same for molecules of different gases is not sufficient to establish the condition of equilibrium of temperature between gases of different kinds, such as oxygen or nitrogen, because when the gases are mixed we have no means of ascertaining the temperature of the oxygen and of the nitrogen separately. We can only ascertain the temperature of the mixture by putting a thermometer into it."[1]

There is, however, an alternative to the assumption that $M_1c_1^2 = M_2c_2^2$, for gases at equal temperatures. Avogadro's hypothesis can be assumed, *i.e.*,

that $N_1 = N_2$
At equal pressures $M_1N_1c_1^2 = M_2N_2c_2^2$
Therefore $M_1c_1^2 = M_2c_2^2$

That is, when gases are in thermal equilibrium, the condition of dynamical equilibrium is fulfilled. Hence, by assuming Avogadro's hypothesis, we can deduce the hypothesis that two systems of molecules in thermal equilibrium are also in dynamical equilibrium, and again, by assuming the latter hypothesis, we can deduce Avogadro's hypothesis.

This puts the proof of Avogadro's hypothesis from the kinetic theory of gases in its true light. The hypothesis is but one out of two hypotheses which are contingent on one another. Either granted, the other can be proved. In such a case, the simpler hypothesis is naturally selected as the basis of reasoning. To the chemist, Avogadro's hypothesis is the simpler of the two. Whether physicists agree to this or not, two conclusions may safely be drawn. First, that it is possible to develop a modified kinetic theory of gases, a fundamental assumption of which is Avogadro's hypothesis. Second, that the transmutation of Avogadro's hypothesis into a law, by means of the kinetic theory of gases, is not a genuine transmutation.

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[1] Camb. Trans., 1879, quoted, Heat, p. 326.

CHAPTER IV.

AVOGADRO'S HYPOTHESIS AS A PRINCIPLE OF CHEMISTRY: THE MOLECULE.

Sometimes by Principle we mean a small particular Seed, the Growth or gradual unfolding of which doth produce an organised Body, animal or vegetable, in its proper Size and Shape.—BERKELEY.

A hypothesis not only serves to explain the facts originally in contemplation, but becomes a principle by being adopted and carried out to its logical conclusions. The first consequence of the adoption of Avogadro's hypothesis is as follows:—

The molecular weights of all gaseous substances are directly proportional to their densities. This means that molecular weights are arrived at, primarily, independently of chemical action.

At the same time, the molecule, whose relative weight is determined apart from chemical change, is made the unit of chemical action. Accordingly, in terms of this molecule, Avogadro gives an account of the facts of Gay-Lussac's law. The formation of two volumes of hydrochloric acid from one of hydrogen and one of chlorine consists in the formation of two molecules of hydrochloric acid from one of hydrogen and one of chlorine; the formation of two volumes of steam from one of oxygen and two of hydrogen consists in the formation of two molecules of steam from one of oxygen and two of hydrogen.

The molecular weight methods are all related to Avogadro's hypothesis; they are (1) the gas density method, (2) the osmotic pressure methods.

1. The determination of the density of a gas leads at once to a knowledge of its relative molecular weight. For a long time molecular weights were measured relatively to hydrogen. As the standard substance, oxygen has great advantages, and is now much used. The standard amount of oxygen is 32 grammes, and is called the gramme molecular weight. The gramme molecular weight of any other substance than oxygen is that weight of it which, in the state of

gas, occupies the same volume as the gramme molecular weight of oxygen, the two being at the same temperature and pressure.

Our knowledge, at first hand, of molecular weights, has been immensely extended by the use of Victor Meyer's vapour density apparatus.

2. Of late years there has been investigated a class of methods related to the osmotic pressure of solutions. The methods are empirical, inasmuch as they involve experiments with substances of known molecular weight. An example of this class is the freezing-point method. In terms of this method, the definition of molecular weight is as follows:—The molecular weight of a substance is that weight of it which produces the same depression in the freezing point of a solvent, as the known molecular weight of some other substance.[1]

There is not only this empirical connection between all osmotic pressure methods and the gas density methods, but something more. Van't Hoff has shown that the osmotic pressure of a dissolved substance is closely analogous to the pressure of a gaseous substance. For equal changes of concentration, or of temperature, the two pressures alter to the same extent. With a given amount of a substance, at the same temperature and volume, the pressure of the substance in the state of gas is equal to the osmotic pressure of the substance when in the dissolved state.

In a very striking way Van't Hoff has tested this identity. Just as work can be done against the pressure of a gas, work can be done against osmotic pressure. Regarding the freezing-point method of molecular weight determination as consisting essentially in the separation of solvent from solution, accompanied by freezing of the pure solvent, Van't Hoff calculates the work done against osmotic pressure, in separating solvent from solution. Thus, a formula for the solvent constant is arrived at, which involves as factors, the temperature of fusion, and the latent heat of fusion, of the solvent. There is good agreement between the constant as found empirically, and as calculated from this formula. The following figures, taken from Walker's Introduction to Physical Chemistry, 1899, p. 329, show the extent of the agreement:—

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[1] It is well known that the dissolved substance must not be an electrolyte.

SOLVENT.	CONSTANT. CALCULATED.	CONSTANT. EMPIRICAL.
Water,	1850	1840
Formic Acid,	2840	2770
Acetic Acid,	3880	3900
Benzene,	5100	4900
Phenol,	7600	7400
Nitrobenzene,	6950	7070
Ethylene Dibromide,	1190	1180

Accurate molecular weight determination by the measurement of gas densities has been carried out in the case of only a few gases. The gas laws are of limited accuracy, Gay-Lussac's law being only an imperfect description of the facts, even in the case of the combination of hydrogen and oxygen. With one volume of oxygen there combine, not two volumes of hydrogen, but, according to Scott 2·00285, to Leduc 2·0037 and to Morley 2·00269.[1] From gas density measurements, therefore, accurate molecular weight data are to be got only by the application of a special correction. The necessity of making such a correction was recognised in 1892 by Rayleigh.[2] A systematic way of making the necessary correction was proposed and successfully applied to certain gases first by Daniel Berthelot.[3]

In general, determinations of gas density are not supposed to give the most accurate molecular weight data. Nearly always, these are got by using the results of gas density measurements in order to interpret the chemical combining weights. Thus, Morley found that 30·3966 g. of oxygen combine with 3·8286 g. of hydrogen and give 34·2261 g. of water; that is, the molecular weight of oxygen, 32 g., combines with 4·0306 g. of hydrogen, yielding 36·0315 g. of water.[4] From the gas density we know that the molecular weight of oxygen being 32, that of hydrogen is about 2, and that of water about 18. Combining these two sets of data, it is evident that 4·0306 is the accurate weight of two molecules of hydrogen, and 36·0315 of two molecules of water. Hence, from this experiment, the molecular weight of hydrogen is 2·0153, and that of water 18·0157.

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[1] Morley, p. 110. [2] Proceedings of the Royal Society, 1892, 50, 461.

[3] Comptes Rendus, 1898, 126, 954. [4] Morley, p. 109.

Yet another illustration may be given of this combination of two sets of data in order to arrive at accurate molecular weights. Hardin found that 0·19631 g. mercuric oxide contained 0·18177 g. mercury, and therefore, by difference, 0·01454 g. oxygen.[1] That is, to form mercuric oxide, the molecular weight of oxygen (32 g.) combines with 400·0 g. mercury. From gas density data we know that the molecular weight of mercury is about 200. Evidently 400·0 is the accurate weight of two molecules of mercury, and the accurate molecular weight of mercury is 200·0.

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[1] Smith. Misc. Collections, 1075, Clarke's Recalculation of Atomic Weights, p. 168.

CHAPTER V.

AVOGADRO'S HYPOTHESIS AS A PRINCIPLE OF CHEMISTRY (continued): THE ATOM.

> *The harmony of a science, supporting each part the other, is and ought to be the true and brief confutation and suppression of all the smaller sort of objections.*—BACON.

The adoption of Avogadro's hypothesis as a principle of chemistry leads, in the second place, to the conclusion that the molecules of many of the elements consist of parts. Consider the molecule of hydrogen. In the formation of hydrochloric acid from its elements, one molecule of hydrogen gives rise to two molecules of acid. Each molecule of acid containing hydrogen, it appears that in this chemical change, the molecule of hydrogen is split in two. In the case of the molecules of chlorine and oxygen, similar reasoning leads to a similar conclusion. Each of these molecules can be split in two.

This is a most important consequence of Avogadro's hypothesis. Returning to the case of hydrogen, it is found, in general, that hydrogen enters into its compounds by half-molecules. Compounds of hydrogen are known, the molecules of which contain, some a half-molecule of hydrogen, some two half-molecules, some three, and so on. No compound of hydrogen being known which contains, per molecule, less than a half-molecule of hydrogen, it is supposed that the molecule of hydrogen consists of no more than two equal parts. Such parts are called atoms.

A protest against the use of the word "atom" has been made by Guthrie. "The heavenly bodies in their orbits are types of the particles of matter which we handle. Call these small parts particles if you please, or call them molecules, but do not call them atoms, do not write *finis* to the book of nature." With the spirit of this all chemists are now constrained to agree. The word "atom," which can hardly be given up, is not now used in the rigid sense to which Guthrie makes objection. Even apart from the analysis of the atom into electrons, the modern conception of the atom is a quite pliable one. The atom is the smallest part of an element which is found to enter into the composition of a molecule. This definition, as an appeal to our experience of molecules, implies a readiness to accept whatever addition to our knowledge of molecules the day may bring forth.

Of the two problems of atomic-weight determination, the first, how to ascertain the experimental data, hardly comes into consideration in this essay. The present question is the other problem, namely, the interpretation of the data. Precisely stated, this problem is the determination of chemical formulæ, or, in the words of Berzelius, "the determination of the relative number of atoms in chemical compounds."

As a preliminary to the determination of formulæ, there is to be considered the question of classification. This may be carried out on chemical or on physical grounds. As a result of experience, a method of classification on physical grounds has been arrived at, which is in accordance with chemical considerations also. This is the method of isomorphism.

Isomorphism is a means of classification essentially; truly isomorphous substances are classed together, those in the same class subsequently receiving the same general formula. Sodium and potassium chlorides being isomorphous, they receive the general formula $M_x Cl_y$.

This implies that isomorphism is a molecular weight method in the first place. Sodium and potassium chlorides being isomorphous, the respective quantities of each which contain the same amount of chlorine are the relative molecular weights. These relative weights are the same, whatever values be assigned to x and y in the formula $M_x Cl_y$ and consequently whatever atomic weights for sodium and potassium may finally be decided upon.

In the second place, in arriving at atomic weights, isomorphism in itself is not sufficient; it affords no means of assigning values to x and y in the formula $M_x Cl_y$. That must be done on other grounds. Isomorphism may be called a subordinate atomic weight method, inasmuch as it does not stand by itself, but must be used in subordination to other methods.

In addition to the method by isomorphism, the atomic weight of an element is determined (1) on consideration of the molecules into which the element enters, (2) from the specific heat of gases, (3) from the specific heat of solids, (4) from the periodic system of the elements. These methods will now be considered in order.

The first of these, the predominant method, is based on the definition of the atom as the "smallest part of an element which is found to enter into the composition of a molecule." It has already been explained. There remains only to consider the extent to which recourse can be had to it.

By this method, the easiest atomic weights to decide are those of the non-metallic elements. They, on combination with one another, form numerous compounds which are gaseous or easy to convert into gas. Hence, of all atomic weights, so far as these depend upon formulæ, those of the non-metallic elements are least subject to uncertainty.

The study of the non-metallic elements in this way reveals the existence of compounds of certain types. They are, for instance, (1) hydrochloric acid, HCl; (2) water, H_2O; (3) ammonia, H_3N; (4) methane, H_4C; (5) phosphoric chloride, Cl_5P; (6) fluoride of sulphur, F_6S. Accordingly there are elements which combine with hydrogen or its equivalent, some atom with atom, some one atom with two, some one atom with three, and so on. This is the basis of the idea of valency. An element which combines with hydrogen atom for atom is said to be univalent, an element one atom of which combines with two atoms of hydrogen, is said to be bivalent, and so on in order, trivalent, quadrivalent, etc.

The case of the metallic elements is harder to solve, their compounds being much less volatile. The difficulty is often overrated, seeing that, for evidence as to the atomic weights of the metals, their compounds with the hydrocarbon radicals methyl, ethyl, etc., might be quoted far oftener than they are. Even apart from these compounds, the molecular weights of a number of metallic compounds have been found. Victor Meyer's vapour density apparatus is very handy for all such purposes. One thing is specially important, namely, to show that there are univalent, bivalent, trivalent, and quadrivalent metals. The following formulæ, for instance, have been established:—(1) KI, (2) $HgCl_2$, (3) $BiCl_3$, (4) $SnCl_4$.

In deciding on the molecular formula of a substance, a knowledge is useful of the specific heat of the substance in the state of gas. There are two definite ways of measuring the specific heat of a gas, the gas being maintained (1) at constant pressure, (2) at constant volume. These two quantities of heat are different, and their ratio for each gas is an important constant of the gas. The ratio is usually denoted by C_p / C_v. The value of this, for substances which consist of two atoms to the molecule, such as oxygen and nitric oxide, is 1·40. The value for sulphuretted hydrogen is 1·31, and for methane 1·27. For more complex molecules, still lower values are got.

The empirical law is, the simpler the molecule, the higher the value of C_p / C_v. Mercury vapour and argon give the value 1·66. This is evidence that the mercury and argon molecules consist of one atom each. By other methods this conclusion regarding mercury is confirmed.

A meaning to the ratio C_p / C_v is given by the kinetic theory of gases. When heat is given to a gas at constant volume, the heat may be used up in two ways, (1) in increasing the motion of the parts of the molecules, (2) in increasing the motion of the molecules as wholes. Let the ratio of these quantities of heat be b. Again, when heat is given to a gas at constant pressure, the heat is used up not only in these two ways, but also, during expansion, in overcoming the external pressure on the gas. Let this quantity of heat be denoted by W. Then $C_p = C_v + W$, so that $C_p / C_v = (C_v + W) / C_v$. It can be shown that this latter ratio equals $1 + \frac{2}{3(1+b)}$.

The larger the number of atoms to the molecule, the larger will be the value of b. At the same time, the nearer does the value of C_p / C_v approach to 1. When the molecule has no parts, the value of b becomes 0, and of C_p / C_v 1·67. The agreement observed here between the theoretical value and the experimental value for mercury and argon is most striking. Armstrong, nevertheless, has passed an adverse criticism upon this method, consideration of which is reserved for the end of this chapter.

The specific heat method for solid elements depends upon Dulong and Petit's law, that the atomic heats of the elements are equal. As usually adopted, this method implies a special definition of the atom, namely, that the atomic weight of an element is equal to 6·4 divided by its specific heat.

The relation between this definition and the definition of the atom as a part of the molecule must be established, otherwise there are two independent definitions of the atom. The necessity of establishing this relation is not generally recognised, the atomic heat law being very often regarded as a plausible thing on the face of it. But why should particles of matter of different kinds have the same capacity for heat, even if the particles are indivisible?

It would be just as plausible to say that the atoms have the same capacity for electricity and to call this a law. On the basis of this law, definite formulæ can be ascribed to the salts of the metals. If potassium iodide is KI, mercuric chloride is HgCl, stannic chloride is SnCl, etc. These formulæ satisfy the law, because they involve equal negative charges on the atoms of chlorine and iodine, and equal positive charges on the atoms of potassium, mercury, and tin. For these compounds, Dulong and Petit's law leads to the formulæ KI, $HgCl_2$, $SnCl_4$. The two laws are incompatible with one another.

Of the two supposed laws, each has defects of its own. A difficulty in the way of accepting the law that atoms have the same capacity for electricity is that there are metals which form more than one chloride. This difficulty may be overcome in a more or less satisfactory way, by ascribing the general formula MCl to the most characteristic chloride selected as such on chemical grounds. In Gmelin's, and also in Gerhardt and Laurent's system of chemistry such a state of things was realised.

Of Dulong and Petit's law the great defect is that the specific heats of the elements are not constant. As the temperature falls, specific heats tend to decrease. Long known in the cases of carbon, silicon, boron and beryllium, this change is now known to go on in the case of many of the metals. The following data, obtained by Tilden,[1] show this:—

Average specific heat.	Nickel.	Silver.
Between +15° and +435°.	0·124.	0·058.
„ −182° „ +15°.	0·084.	0·052.

Besides this, in the case of many of the metals which are supposed to be instances of conformity to Dulong and Petit's law, the deviations from the constant 6·4 are considerable, and even, in certain cases, amount to 10 per cent.

These defects apart, any one of these laws, taken by itself, is as plausible as the other. The laws are also incompatible with one another. A decision between them in favour of Dulong and Petit's law is given by Avogadro's hypothesis.

To sum up, the specific heat method is not an independent but a subordinate atomic weight method. Dulong and Petit's law does not recommend itself, nor stand on its own footing, but requires proof like any other law. Assumed to be true, the law leads to the recognition of univalent, bivalent, trivalent, and quadrivalent metals. As a matter of chemical history, the law has been much used in fixing the atomic weights of the metals. It is therefore of particular importance to test the law not for non-metals only, but also in the cases of uni-, bi-, tri-, and quadri- valent metals. For instance, the atomic weights of potassium, mercury, bismuth and tin can be arrived at from a knowledge of the composition and the vapour densities of their compounds. For each of these metals the atomic heat is not far from 6·4. Nevertheless, it is quite the custom to regard Avogadro's hypothesis and Dulong and Petit's law as independent of one another. Tilden says, "It is interesting and important to note that whenever the two methods, based on the use of the law of Avogadro on the one hand and that of Petit and Dulong on the other, can be applied to the same element the results agree."[2]

As a matter of history, Dulong and Petit's mere forecast of 1819 was not accepted as a law. Tilden remarks, "The principle asserted by Petit and Dulong remained unapplied and almost unnoticed, save casually as a matter of curiosity, down to the present generation."[3] This remark conveys a somewhat wrong impression of the facts of history. Berzelius, in 1826, and Dumas, in 1836 (in the "Leçons sur la Philosophie Chimique"), accepted the law with reserve. In 1827, in the "New System of Chemical Philosophy" (pp. 293-4) Dalton criticised it adversely. In 1843, all the exceptions to the law, in Gmelin's system and in Berzelius', were carefully tabulated by Gmelin in the Handbook. But if the mere assertion of Dulong and Petit's law carries conviction with it, men of science must have accepted the law at once. It was accepted as soon as Cannizzaro reconciled it with Avogadro's hypothesis.

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[1] C. N., 87, 100. [2] Short History, p. 74. [3] Op. cit., p. 75.

Trustworthy atomic weight data available, the classification of the elements according to their atomic weights is possible. The classification, once arrived at, can be used in turn in the criticism of atomic weights. Such a classification is the periodic system, which originated with Newlands (1864), and was further developed by Mendeleeff (1869) and Lothar Meyer (1869).

As an atomic weight method, the periodic system has been made use of in two distinct ways. In the first place, it has been used in deciding between alternative formulæ for a compound, a formula being accepted or rejected, according as the corresponding atomic weight fits well or ill into the periodic system. That this is a sound atomic weight method there is no reason to doubt. It was used by Newlands in deciding on the adoption of the atomic weight which is now generally approved for glucinum. A similar use of the periodic system was made by Mendeleeff, for instance, in the case of uranium, and by Lothar Meyer in the case of indium.

The periodic system has also been used in criticising the numerical accuracy of the atomic weights. Mendeleeff criticised the data which were at one time accepted for gold, iridium, platinum, and osmium. Having shown that the arrangement of these metals according to their atomic weights was not the same as the arrangement according to physical properties, he expressed the conviction that the atomic weight data were wrong. Subsequent investigation showed that Mendeleeff's conjectures were right, the atomic weights to which he took exception having been considerably in error. Nevertheless, this use of the periodic system is open to suspicion. Time has shown that the arrangement of the metals in the order of their atomic weights is not quite identical with the arrangement according to properties. Numerous recent investigations concur in assigning to tellurium a higher atomic weight than iodine. Yet tellurium, on all other grounds, might be expected to have a lower atomic weight than iodine, and actually, in the periodic system, is always placed before iodine. Such an anomaly is not to be ignored. Also, argon stands in a similar relation to potassium, and nickel to cobalt.

Accurate molecular weight data are a preliminary to arriving at accurate atomic weight data. Given molecular weights, in order to arrive at atomic weights, a knowledge of molecular formulæ is needed. From the fact that one molecule of oxygen gives two molecules of water, the oxygen molecule of weight 32 has the formula O_2, so that the atomic weight of oxygen is 16. The consideration that two molecules of hydrogen give two molecules of water is no reason for supposing that the hydrogen molecule is like the oxygen molecule in consisting of two atoms. That conclusion is arrived at from the fact that one molecule of hydrogen gives two molecules of hydrochloric acid. The hydrogen molecule having the weight 2·0153 (as the result of a particular experiment, see previous chapter, p. 28), the weight of the hydrogen atom is 1·0076.

The molecular weight of mercury being 200·0, the mercury molecule has never been divided, so that 200·0 is also the atomic weight of mercury.

When the atom of the element is divided into electrons, a new order of matter is reached. Again, the conception of the atom implies an appeal to experience, and experience is always being extended. None of the atomic weight methods is final. However, the majority of chemists, I presume, feel satisfied that the supposed atoms of the elements are really at the limit of division of ordinary matter. Hardly any other view is possible, because the atomic weight methods, taken as established, and applied to any particular case, agree well with, and hardly ever contradict one another.

As has been shown, the C_p/C_v method of studying the composition of molecules has a double basis, (1) empirical, (2) the kinetic theory of gases. In recent years it has found independent justification. As made use of by Rayleigh, Ramsay, Travers, the method leads to atomic weights for argon and its congeners, which fit remarkably well into the periodic system.

In spite of all this testimony, Armstrong maintains that the "element most nearly resembling argon is nitrogen," and that argon and its congeners therefore consist of diatomic molecules.[1] A test of the soundness of this analogy between nitrogen and argon is afforded by its results upon chemical classification.

For the chemical elements, Armstrong has a classification of his own. Helium is put in a column by itself; neon, krypton and xenon are put in another column along with indium; argon is put in the same column as iron, nickel, and cobalt, away from nitrogen.

These results are by themselves a stultification of the supposed analogy between argon and nitrogen. Why should nitrogen and argon be classed apart from one another, unless for the reason that argon does not resemble nitrogen? Surely classification means the putting asunder of things that are unlike one another, and the bringing together of things that resemble one another. In the same class Armstrong puts fluorine, chlorine, manganese, bromine, and iodine. He puts helium, neon, argon, and nitrogen in four different classes. This is tantamount to saying that these four elements do not resemble one another. It is therefore quite possible that while the molecule of nitrogen is diatomic, the molecules of helium, neon, and argon are something else.

Armstrong, supposing that the argon molecule is diatomic, suggests that if the two argon atoms within the molecule "are gifted with a very high degree of mutual affinity, the molecule might well be so stable that no internal work is done on heating" the gas, when the C_p/C_v method, of course, must fail.[1] On this ground of pure conjecture, Armstrong proceeds to reject the method.

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[1] E. B., vol. 26, Article Chemistry.

Admitting that this conjecture is possibly right, one may go on to enquire why the same line of argument should be taken only in the case of argon and its congeners. It is easy enough to take it further. No atomic weight method is final. The mercury molecule *may* consist of atoms which are "gifted with a very high degree of mutual affinity," and it "*may* well be so stable that no internal work is done on heating" it—so stable, indeed, that no chemical agent is able to separate the atoms. The carbon atom *may* consist of smaller atoms gifted with a very high degree of mutual affinity, so that the atomic weight of carbon is a fraction of 12. Speculation may be continued without end on these lines.

The smaller atoms which make up what we know as the carbon atom may not be all of the same kind, so that carbon is not an element. The truth is, that if Armstrong's argument be allowed, all atomic weights are uncertain. If his method be adopted, the atomic weights, one and all, are anything you please.

The recognised antidote to speculation is experiment. Armstrong's criticism, being purely speculative, does not even touch the empirical proof of the C_p/C_v method. With monatomic mercury the ratio got is 1.66, with polyatomic molecules 1.41 or less. Until a molecule known to be polyatomic is found to give the ratio 1.5 or higher, the empirical proof remains untouched.

CHAPTER VI.

THE MOLECULAR FORMULÆ OF THE ELEMENTS.

The hypothesis that equal volumes of different gases under the same conditions contain equal numbers of molecules is rightly ascribed to Avogadro. Certainly, his claim to the hypothesis is not to be based upon the mere enunciation of the hypothesis by him in 1811. In that particular he was forestalled by Dalton in 1808. Later on, independently of Avogadro, other men of science formulated the hypothesis. Ampère took it into consideration in 1814, Dumas in 1827, Prout in 1834, Gerhardt and Laurent in 1842, Krönig in 1855, and Clausius in 1857.

Avogadro has the distinction of having been the earliest of men of science to adopt this hypothesis, consequences and all. The hypothesis is Avogadro's beyond dispute, in the sense that he went on to apply the hypothesis to all the experimental data available, and that he was "not afraid of inferences."

A characteristic feature of modern chemistry is the distinction that has been established between the molecule and the atom of the element. Such a distinction was unknown, and is even foreign to Dalton's atomic theory. Avogadro, as a deduction from his hypothesis, showed that the molecules of hydrogen, oxygen, nitrogen, and chlorine consist of two atoms each. He came to the same conclusion regarding the molecules of carbon and sulphur unsupported by experimental data, and relying solely upon analogy.[1]

Avogadro was far in advance of his times. In 1811, interpreting by means of his hypothesis the experimental data then available, he had arrived at what are substantially the modern views regarding the molecules of the following substances:—water, hydrogen, oxygen, ammonia, nitrogen, nitrous oxide, nitric oxide, hydrochloric acid, chlorine, sulphur dioxide, sulphur trioxide, and carbon dioxide. To this list may be added the following substances, considered in the paper of 1814, namely, marsh gas, olefiant gas, phosgene, sulphuretted hydrogen, and carbon bisulphide. For instance, Avogadro says (in 1811), ". . . the integral molecule of water will be composed of a half molecule of oxygen, with one molecule, or, what is the same thing, two half molecules of hydrogen."[1]

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[1] When relying upon analogies, Avogadro made many mistakes. In 1814, his conclusions concerned the metals chiefly: here, experimental data being absent, he went astray. Whenever the necessary data were available, Avogadro was unerring.

In 1814, Ampère came to conclusions somewhat similar to Avogadro's concerning the molecules of nitrogen, oxygen, etc., and on similar grounds. The fact is not to be ignored that Ampère's suggestions coincide with modern views less closely than Avogadro's. Ampère did not make the explanation of Gay-Lussac's law his sole object. The introduction of other considerations led to complications. Thus he supposes that the molecules of hydrogen, oxygen, and nitrogen are tetratomic. Again, experimental data obtained by Dumas in 1825 led him to the conclusion, for instance, that the molecule of oxygen is diatomic and the molecule of phosphorus tetratomic. Dumas was brought to withdraw this and suchlike conclusions, so unfavourably were they received.

Prout, in 1834, unaware of the views of Avogadro, Ampère, and of Dumas, on consideration of the physical properties of gases, formulated and adopted Avogadro's hypothesis. In consequence, he regarded the molecules of oxygen, hydrogen and chlorine, for instance, as capable of being halved. On account of the composition by volume of water and of hydrochloric acid, Prout concludes:—"Not only the self-repulsive molecule of hydrogen, but also the self-repulsive molecule of chlorine, must be double at least, like the self-repulsive molecule of oxygen; and the same double state of the molecules might be shown with respect to other gaseous bodies." Prout, entering like Ampère into further complications, departed from the simplicity which is the merit of Avogadro's conclusions without gaining anything in return. "The self-repulsive molecules of oxygen and of hydrogen are at least double; but the probability is, that they are in reality much more compounded." See Prout's Bridgewater Treatise, 1st ed., 1834, pp. 62-4, 123-35, or 4th ed., 1855, pp. 76-8, 101-12.

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[1] A. C. R., 4, 32. "Ainsi, la molécule intégrante de l'eau, par exemple, sera composée d'une demi-molécule d'oxigène avec une molécule, ou, ce qui est la même chose, deux demi-molécules d'hydrogène." Delamétherie, 73, 61.

Next, Gerhardt and Laurent adduced evidence that the chlorine molecule, for instance, consists of two atoms. Clausius, in 1857, independently, on the ground of the theory of heat, came to a similar conclusion. Finally, in 1858, Cannizzaro formulated the modern doctrine that the molecule of an element may be monatomic or polyatomic.

At the present time not only diatomic, but monatomic, triatomic, and tetratomic molecules are known. The elements whose molecules are monatomic are:—(1) the metals. This is known (a) by vapour density determinations in the cases of mercury, zinc, cadmium, sodium, and potassium; (b) by experiments with the "freezing-point" method, using a metal, tin, for instance, as the solvent. (2) Argon and its congeners. This is known from the C_p / C_v data.

The principal elements which have diatomic molecules are hydrogen, oxygen, nitrogen, and the halogens. Of tetratomic molecules, the cases of phosphorus and arsenic may be given.

Some elements, it is known, form more than one kind of molecule. Oxygen gives ozone, the only known molecule of an element which is triatomic. There is reason to believe that the halogens can exist as monatomic molecules. In the case of iodine, the evidence is conclusive that at high temperatures the diatomic molecule breaks up into two monatomic molecules.

Divers does not accept these views on the molecules of the elements. He says, "Unfortunately Avogadro's hypothesis does not hold good in the case of not a few simple substances, and it seems impossible from the chemical point of view, and consistently with the molecular theory, to admit that, because the gas volume has only half the expected mass, the chemical molecule of sodium or mercury is not bipartite like that of hydrogen or oxygen, and chemically equal to either."[1] Divers apparently seeks to maintain that the molecule of the element is essentially "bipartite" or diatomic.

As to the mercury molecule, it is very doubtful if any other chemist than Divers holds that it is bipartite. Not only so, but the diatomic molecule of the element is no longer regarded as the predominant type. Reference to Frankland and Japp's "Inorganic Chemistry," 1884, p. 29, Ramsay's "Modern Chemistry," theoretical part, chap. 5, Erdmann's "Lehrbuch der Anorganischen Chemie," 1900, pp. 38-42, 71-73, and Tilden's "Chemical Philosophy," 1901, pp. 8, 87-88, shows that the existence of tetratomic, triatomic, and monatomic molecules of the elements receives from chemists practically universal recognition. These conclusions regarding the molecules of the elements being based on Avogadro's hypothesis, it is clear that in modern chemistry, this hypothesis has a wider currency than Divers has yet recognised.

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[1] Divers, p. 12.

CHAPTER VII.

AVOGADRO'S HYPOTHESIS IN RELATION TO "PURELY CHEMICAL" METHODS.

Was fruchtbar ist, allein ist wahr.—GOETHE.

The fundamental hypothesis of chemistry is Avogadro's hypothesis. The molecule, whose relative weight is determined on the basis of this hypothesis, is the unit of chemical change. The atom is a subordinate idea; it is deduced from the idea of the molecule. The atom is the smallest part of an element which is found to enter into the composition of a molecule. In this definition of the molecule, and in the subordinate definition of the atom, there is the possibility of a synthetic philosophy of chemistry which, moreover, can be brought into co-ordination with physics. The laws of combination in multiple and in reciprocal proportions appear as deductions from the idea of the atom.

Not as a believer in atoms and molecules, but from a purely critical standpoint, Ostwald takes another view from that just given, of the relation between the molecule and the atom. He holds that modern chemistry is a product of two hypotheses—the atomic hypothesis due to Dalton, and the molecular hypothesis due to Avogadro.[1]

This is partly a historical question, and, as such, it will be considered in the second part of this essay. For the present, one obvious objection to Ostwald's view may be pointed out: the unity of chemistry is at stake, just as it was when the supposition was made that inorganic and organic chemistry were two independent sciences.[2] The view that the molecular and atomic hypotheses are independent of one another involves the possibility of molecular and atomic weights which have no connection with one another. If the independence of the molecule and the atom is a tenable doctrine, it has never been worked out to its logical conclusion. Reduced to practice, its results are likely to be cumbrous and highly unpopular. The sanction of chemists never has been given, and is never likely to be given, to a molecular weight system and an atomic weight system which are independent of one another.

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[1] Ostwald, pp. 146-150.

[2] This was Dumas' suggestion. Klassiker, 30, 59.

There is, in fact, no advantage whatever in regarding the atomic and the molecular hypotheses as independent of one another, and no need so to regard them. A relation between them has been shown in this essay, it being maintained that molecules are the source of our knowledge of atoms, and molecular weights of our knowledge of atomic weights. In a similar way it might be shown that our knowledge of radicals is based on our knowledge of molecules.

In addition to the molecular and atomic weight methods the dependence of which on Avogadro's hypothesis has been established, there are certain so-called "purely chemical" methods. These methods, which are a strong feature of organic chemistry, take into consideration the chemical reactions of a substance, a decision being come to thereupon regarding the formula of its molecule. I understand Divers to go so far as to assert that "purely chemical" methods can be made use of, so as to furnish a way of measuring matter, which is quite independent of all other ways, and at the same time, that these "purely chemical" methods are sufficient as a basis for chemical theory. Such is the interpretation which I put upon the following passages:—

"The chemical equality of quantities of different substances is independent of all other relations of equality between them,"[1] and therefore, presumably, independent of the fact that in the gaseous state, they occupy the same volume.

"It is then only as colligated equalities, established by experiment, that gaseous volumes, osmotic pressures, and other properties of substances come into consideration, first as enforcing the truth of the conception of the indicated quantities as equal, and then as the means of molecular measurement without resort to chemical change. . . . It is nearly always through recourse to physical methods that the molecule is first ascertained, and then through the molecule the certainty acquired that some particular action is a single one, thus reversing the normal order of things, which undoubtedly is that the molecule in chemistry, however it may have been first determined, is recognised as such by being what it is in chemical change."[1]

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[1] Divers p. 7.

Thus Divers regards the molecule as a conception by itself, and the physical means which are taken of arriving at the molecular weight as so many short cuts which, if need be, the chemist can do without.

Divers' theory is, I believe, that all chemical changes, when fully analysed, are reactions *between pairs* of molecules. "With hardly an exception, all that is stated concerning the nature of those chemical changes in which two or three substances become one, or one becomes two or more, is based upon notions derived from the study of double decomposition."[2] "The quantities of the four substances of a single interaction are all equal and are molecules; but the quantities of substances are not equal in other interactions. These others are treated as the simultaneous occurrence of two or more single interactions, which they can always be represented and sometimes demonstrated to be. . . . The expression 'two or more molecules of a substance' has a meaning only as indicating the number of simultaneous or successive single interactions which have led to the conversion of certain substances into others."[3]

In this essay it is maintained that the basis of our knowledge of molecules is Avogadro's hypothesis. If Divers' theory of chemistry inevitably leads to the strictures which he has passed on Avogadro's hypothesis in its application to the determination of the molecular formulæ of the elements, so much the worse for the theory, because, as I have shown in Chapter VI., nearly all chemists on this very point accept the guidance of Avogadro's hypothesis.

Even apart from this, there are two main objections to Divers' version of the theory of chemistry, namely, in regard to his contentions (1) that chemical changes go on between pairs of molecules, (2) that chemical formulæ can be determined independently of Avogadro's hypothesis.

Much interest has been taken of late years in the mechanism of chemical reactions. The advances which have been made in our knowledge of the progress of chemical change, have arisen largely by the application of Guldberg and Waage's law of mass action. On the basis of this law, in fact, there can be established a general way of finding the number of molecules that take part in a chemical reaction. The results show that chemical reactions are not what they seemed; a reaction, apparently complicated, is found to take place in simple stages. On the other hand, a reaction sometimes turns out to be more complex than it was thought to be.

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[1] Loc. cit., p. 8. [2] Loc. cit., p. 10. [3] Loc. cit., pp. 15-16.

Far from reducing all chemical changes to a matter of reactions between pairs of molecules, modern chemistry recognises such reactions as only one of several kinds. A reaction that goes on by a change in single molecules is said to be monomolecular, one between two molecules a bimolecular reaction, one between three molecules a trimolecular reaction.

The following instances are given by Van't Hoff[1]:—

(1) A monomolecular reaction—the decomposition of arsine by heat. The equation is $AsH_3 = As + 3H$, the formation of the molecules As_4 and H_2 being subsequent changes.

(2) A bimolecular reaction—the saponification of ethyl acetate. The equation is $CH_3COOEt + NaOH = CH_3COONa + EtOH$.

(3) A trimolecular reaction—that between ferric and stannous chlorides. The equation is $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

I am at a loss to see how the existence of monomolecular and of trimolecular reactions is to be reconciled with the assumption that chemical reactions are essentially bimolecular. Divers' theory can be accepted only on the condition that Van't Hoff's teaching is ignored.

Further, it is often asserted that chemical reactions are sufficient to decide the nature of the molecule. Divers refers to "the normal order of things, which undoubtedly is that the molecule in chemistry, however it may have been first determined, is recognised as such by being what it is in chemical change." Far from this being "undoubted," Lothar Meyer has noticed in the most pointed way the attempts of chemists to do without Avogadro's hypothesis. "That the study of chemical reactions for the determination of molecular weights without the aid of Avogadro's hypothesis is very deceptive and thoroughly inadequate is seen from the fact that molecular weights which were quite different from Avogadro's were for many years used in representing chemical reactions, and were universally regarded as satisfactory."[1]

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[1] Van't Hoff, Vorlesungen, erstes Heft, die Chemische Dynamik, 1898, pp. 185-191.

Again, Lothar Meyer refers to the "purely chemical" methods as follows:—"The fact that the general adoption of the molecular weights, determined by Avogadro's law, was only brought about after a careful examination of numerous chemical transformations has led to the erroneous conclusion that the weight and composition of the molecule of any substance can be determined by means of chemical reactions alone, without the knowledge of the vapour density of the substance."[2] Lothar Meyer then proceeds to demonstrate that the "purely chemical" methods, from a logical standpoint, are failures.

Nevertheless, in accordance with Divers' view, Tilden states, ". . . independently of the existence of vapourisable compounds and of any application of Avogadro's hypothesis, the atomic weight may in some cases be determined by appeal to purely chemical considerations."[3] In the case of water, the facts and the argument are well known; the displacement of the oxygen in water takes place in one stage, the displacement of the hydrogen by the agency of potassium, in two distinct stages. In explanation of these particular changes, the formula OH is undoubtedly not so good as H_2O.

This is a test case. If the formula H_2O for water can indeed be established independently of Avogadro's hypothesis, then it is impossible to maintain that the hypothesis has the standing in chemistry which this essay claims for it. If, on the contrary, the hypothesis is indispensable in order to establish the formula, then the conclusion, that Avogadro's hypothesis is the fundamental hypothesis of modern chemistry, is greatly reinforced.

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[1] "Modern Theories of Chemistry," trans. by Bedson and Williams, 1888, p. 13.

[2] Op. cit., p. 12.

[3] Chemical Philosophy, p. 79.

The above method of proof must not be confined to water. On hydrofluoric acid the action of potassium is similar to its action on water—the hydrogen is expelled in two stages; no reagent is known which expels the fluorine in two stages. Nevertheless, hydrofluoric acid receives the formula HF, or H_2F_2 (F = 19), but never H_2F (F = 38). It appears that the proof which is good enough for water is not good enough for hydrofluoric acid.

For rejecting the analogy just detailed, between the reactions of water and hydrofluoric acid, there can be found an excuse, if not a reason. This is, that the two intermediate products, potassium hydroxide and acid potassium fluoride, on being heated, behave differently. The fluoride yields hydrofluoric acid, but the hydroxide does not yield water.

Another reaction of water tells a different tale; potassium is not the only substance which displaces the hydrogen in water. By the agency of calcium it is possible to get from water a product, calcium oxide, which is free from hydrogen. True, there is an intermediate product, calcium hydroxide, but this, on being heated, loses water and yields calcium oxide. The analogy with hydrofluoric acid is complete. For water, the OH formula, as an explanation of the reaction with calcium, is better than the formula H_2O; this is confirmed by the analogy with hydrofluoric acid. What occult influence is at work, which determines that this reaction shall be ignored and that reaction considered? Why accept the formula HF and reject the formula OH? The answer, I suspect, must be that any formula which happens to be at variance with Avogadro's hypothesis is, *ipso facto*, rejected.

Nor is this all. Weighty as these objections to the "purely chemical" method are, they may be waived, and still the method remains open to criticism. The chemical equations for the formation of potassium hydroxide are:—

Taking the formula OH, $K + 2OH = KOOH + H.$ (1)
" " H_2O, $K + H_2O = KOH + H.$ (2)

Even if the ionic hypothesis does involve a return to the equation $K + H_2O = KOH + H$, it is not against the adherents of that hypothesis that there is any need to assert the importance in chemistry of Avogadro's hypothesis. The ionic hypothesis, as defined by Arrhenius, is based on the Van't Hoff-Avogadro theory of solution, which is simply an extension of Avogadro's hypothesis to dilute solutions.

Equation (2), being simpler than (1), is doubtless to be preferred. Yet neither of these equations is used now—(see footnote, p. 48).

The equation that is used is:—

$$2K + 2H_2O = 2KOH + H_2. \quad (3)$$

Of these equations, (2) is still the simplest. Even equation (1), which involves the fomula OH, is simpler than (3), the current equation.

Here, at every turn, the principle of simplicity seems to be compromised. Yet the explanation of all these perplexities is easy. The truth is, that the "purely chemical" proof of the formula of water, as given above, is out of date. It holds good only while the distinction, now established, between the atom and the molecule of hydrogen is ignored. That distinction, of course, is an immediate consequence of the adoption of Avogadro's hypothesis. In the current interpretation of chemical reactions there is a great principle at work. The condition of simplicity is saved, and the testimony of conflicting reactions is reconciled by the consistent application of Avogadro's hypothesis.

So far, the two positions which have been maintained in this essay are: (1) that Avogadro's hypothesis may not "be regarded as a well-established truth," but remains a hypothesis, (2) that Avogadro's hypothesis being almost universally accepted by chemists has so many fruitful issues that it is the "very basis and corner-stone" of chemistry. It is the basis of our knowledge of molecules and radicals and atoms. Molecular weights being ascertained, and then atomic weights, the periodic system becomes possible. The chief issues of the hypothesis are the molecular theory, including the modern theory of solution, the atomic hypothesis, the doctrine of valency, and the periodic system—the last a perpetual source of speculation and experiment. "Was fruchtbar ist, allein ist wahr."

PART II.

The Standing in Chemistry of Dalton's Atomic Theory.

CHAPTER VIII.

INTRODUCTION.

> *Quoi, mes pères, leur dis-je, c'est se jouer des paroles, de dire que vous êtes d' accord à cause des termes communs dont vous uses, quand vous êtes contraires dans le sens. Mes pères ne repondirent rien.*—PASCAL.

The first part of this essay consists of an enquiry into the standing in chemistry of Avogadro's hypothesis. The distinction between law and hypothesis recognised, it is shown that the term Avogadro's "law" is a misnomer. The molecular theory of chemistry consists of a development of Avogadro's hypothesis. In this way the hypothesis has the following issues, the doctrine of radicals, an atomic hypothesis, the doctrine of valency, and the periodic system of the elements. The second part of this essay is devoted to the consideration of the standing in chemistry of Dalton's theory.

For raising the question of the standing in chemistry of Dalton's atomic theory, a justification lies in the discrepancies between the opinions of chemists on this very subject. Divers' verdict, already quoted, is, that "the theory of chemistry, with all its modern developments, is indisputably the atomic theory of Dalton." According to Pattison Muir, "the modern molecular theory of matter is not identical with the atomic theory of Dalton; it is based on evidence of a different kind, it is essentially a physical and dynamical theory."[1]

On this question few of the chemists who take a view favourable to Dalton have expressed themselves more explicitly than Thorpe. His words are:—"Whatever may be the ultimate fate of the theory which found deliberate expression in the 'New System of Chemical Philosophy,' . . . it is certain that the ages to come will reckon it as the central, dominant conception which has actuated the chemistry of the nineteenth century. The characteristic feature of the chemistry of our time is, in a word, the development and elaboration of Dalton's doctrine; for every great advance in chemical knowledge during the last ninety years finds its interpretation in his theory."[1]

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[1] Principles of Chemistry, 1884, p. 30.

Again, Ostwald, having discussed the atomic hypothesis, and going on to discuss the hypothesis of Avogadro, speaks as follows of the relative importance of the two hypotheses. "Just as the laws of weight in chemical processes, so also the laws of volume in the interaction of gaseous substances have given rise to mechanical hypotheses, which have played a similar though not so important a part in the development of chemistry as the atomic hypothesis."[2] Here Ostwald, regarding chemistry as the product of two independent hypotheses, the atomic due to Dalton, and the molecular due to Avogadro, gives the palm to Dalton.

Thus Divers, Thorpe, and Ostwald are agreed in thinking that Dalton's ideas have been valid throughout nineteenth century chemistry. A question which such authorities are agreed upon might, without "excessive awe of authority," be regarded as settled. I should so regard the present question, were it not for one circumstance that looks suspicious. This concordance of opinion as to the validity of Dalton's ideas is not accompanied by uniformity in stating what his ideas are.

Avogadro's hypothesis readily admits of precise definition, on which account it was taken into consideration in this essay before Dalton's atomic theory. In considering the standing in chemistry of Dalton's theory, there is, in fact, a difficulty at the outset. Strange as it may seem, the difficulty is neither more nor less than to find out what the theory really is.

Divers' account of Dalton's atom is as follows:—"Dalton gave us the conception of the molecule, though confused with that of the atom,"[3] and again, "Dalton's atoms were both the atoms and the molecules of present-day chemistry, but much more the latter than the former."[1]

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[1] Thorpe, p. 516. [2] Ostwald, p. 148. [3] Divers p. 8.

A different view of the Daltonian atom is taken by Ostwald. He regards chemistry as the product of the molecular hypothesis, due to Avogadro, and the atomic hypothesis, due to Dalton. So that, for Ostwald, the Daltonian atom is the modern atom.

Thorpe, in his "Manual of Inorganic Chemistry," appears to take a view similar to Ostwald's. After detailing the laws of chemical combination by weight, Thorpe explains[2] the atomic theory, and refers to the indivisibility of the atom. With all this he associates the name of Dalton. The treatment of the subject of the atom in such a way surely affords a presumption that Thorpe holds Dalton's atom to be the modern atom.

All this does not make it easier to find out what Dalton's theory is. Doubtless, the chemists who hold with Thorpe and Ostwald that Dalton's atom is the modern atom are the more numerous body. On the other hand one feels instinctively, so much is the molecule the predominant idea in modern chemistry, that Dalton's ideas have lost their ascendency, unless his atom is the modern molecule.

The case stands thus: there are two questions at issue—first, what Dalton's theory is, second, the question as to the standing of the theory. The first question is the crucial one; it answered, the rest is easy. The odd thing is that chemists should show much greater unanimity about the second question than they do about the crucial one. Thorpe regards Dalton's atomic theory as "the central, dominant conception" of nineteenth century chemistry. Divers regards modern chemical theory as "indisputably the atomic theory of Dalton." Ostwald regards chemistry as the product of two hypotheses, of which Dalton's atomic hypothesis is the more important historically. Here, more or less, Thorpe, Divers, and Ostwald are at one. It is on the crucial question that they are at variance.

Divers and Ostwald agree that in chemical theory the molecule is important; on this point, in his eulogy of Dalton,

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[1] Loc. cit., p. 15. [2] Non-metals, 1896, pp. 41-46.

Thorpe is silent. Again, Dalton's atom, according to Divers, is the modern molecule; the modern atom, according to Ostwald.

"Who shall decide when doctors disagree?" Much as a definite understanding about the rudiments of chemistry is to be desired, it is plain that to such an understanding chemists have not yet come. Till they do, and until the "glorious uncertainty" as to what is Dalton's theory is somewhat lessened, I fail to see how positive statements, that "the ages to come will reckon Dalton's theory as the central, dominant conception which has actuated the chemistry of the nineteenth century," and that "the theory of chemistry, with all its modern developments, is indisputably the theory of Dalton," can be received with anything but distrust. How can chemists maintain, as a foregone conclusion, that Dalton's theory is predominant in chemistry, no matter what the theory be?

In considering scientific doctrines, some definite conception or other of science must be kept in view. In the course of the argument, as a guiding principle or touchstone, I use the dictum that "science is measurement." This dictum can be illustrated by considering the ways of treating the ideas of time and space. Science, so understood, has little to do with definitions of time and space in the abstract. The man of science proceeds by defining standards, which serve in the measurement of time and space.

Observe the bearing of this conception of science on chemistry as the science of molecules and atoms. The scientific conception of the molecule is that which implies a means of measuring molecules. This is just what Avogadro's hypothesis comes to; it implies a way of measuring the relative weights of different molecules. Moreover, molecular weights once ascertained, atomic weights can be arrived at. Hypotheses which lead only to uncertainty about molecular and atomic weights are, for that very reason, inferior in scientific value to Avogadro's hypothesis.

Here the questions at issue become sharp enough. There is first the question, what are the points of difference between Avogadro's hypothesis and Dalton's theory? And the further question, can Dalton's theory rival Avogadro's hypothesis as a basis for the cardinal doctrines of chemistry: is it as good as the hypothesis, or not so good, or better?

This two-fold problem, apparently plain, is entangled by another consideration. Thorpe is willing to entertain the conjecture that Avogadro's hypothesis should be ascribed to Dalton. His words are, "This perhaps is not the time and the place to discuss the question of whatever claims John Dalton may have to be the first to recognise the fundamental truth embodied in the statement that gases, under comparable conditions, contain in equal volumes equal numbers of molecules, whatever may be their nature and their weight."[1] I am not aware that Thorpe has ever found occasion for the discussion of this question. Considering that this hypothesis is regarded by many chemists as the corner-stone of chemistry, and that almost all chemists ascribe the hypothesis to Avogadro, it is strange that Thorpe should throw out vague hints as to Dalton's claims to the hypothesis, and be content to leave the matter there.

The original exponent of Dalton's claims to the hypothesis is Debus. With no uncertain sound, he asserts and maintains that the said hypothesis was the germ and guiding principle of Dalton's theory.[2]

This is a subject of great interest. What Debus maintains is that Avogadro's hypothesis should be ascribed, not to Avogadro, but to Dalton. If this be so, there is no material disagreement between those who maintain, with Cooke, that Avogadro's hypothesis is the fundamental hypothesis of modern chemistry, and those who maintain, with Divers, that "the theory of chemistry, with all its modern developments, is indisputably the atomic theory of Dalton." If Debus' contention be at all sound, those who side with Cooke against Divers find themselves stultified. Proofs, one and all, that the so-called Avogadro's hypothesis is fundamental in chemistry, only redound to the credit of Dalton. If, on the other hand, Debus should prove to have been mistaken, then the disagreement between Cooke and Divers is material after all.

In order to come to a decision on the question, what is the standing of Dalton's theory in chemistry, the design of this part of the essay is, first, to ascertain, as exactly as possible, what is the essence of his theory, and at the same time to consider the above contention of Debus; next, to consider the test of the theory which experience supplies, namely, the history of the chief systems of chemistry; lastly, an attempt will be made to ascertain how much of Dalton's teaching is still in vogue.

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[1] Thorpe, p. 511. [2] Zeitschrift, 20, 359, 20, 325, 20, 266.

CHAPTER IX.

THE ESSENTIALS OF DALTON'S THEORY.

Les choses valent mieux toujours dans leur source.—PASCAL.

In this chapter the object being to arrive at the sum and substance of Dalton's theory, the design is to consider first of all what Dalton understood by an atom; then, to show the nature of the Daltonian atom in the clearest possible light, by comparing it with the modern molecule and with the modern atom. Consideration will be given next to Dalton's system of chemistry, and finally to Debus' contention that Avogadro's hypothesis enters into the structure of Dalton's system.

In carrying out this design, there are features of Dalton's theory on which I shall not dwell. He was the great pioneer of a scientific atomic theory. From pioneers, infallible instinct and unfailing accuracy are not to be expected. There are, in fact, certain accidental features of Dalton's system which are liable to prove a mere distraction to the inquirer. The important facts of the case are obscured if the inquirer is misled into laying stress on these features.

For the present purpose an inquiry into the genesis of the theory is unnecessary. This is fortunate, because the trains of thought which Dalton is said to have followed in forming the theory are so numerous that they can hardly all be genuine. Here it is sufficient to say that he had the matter under almost constant consideration between 1803 and 1808. He embodied the theory in the "New System of Chemical Philosophy," of which volume 1, part 1, was published in 1808, volume 1, part 2, in 1810, and volume 2, part 1, in 1827.

I have already had occasion (Chapter III.) to comment on Divers' readiness to sever all connection between the "mechanical," or kinetic theory of matter, and the atomic theory of chemistry. Admitting that Dalton's "mind was fully possessed with the ancient and current belief . . . that substances are made up of minute, discrete particles," Divers, nevertheless, formulates a theory which is "divested of all reference to the physical constitution of matter," and this he advances as being the essence of the Daltonian theory. I have pointed out that to call a theory which makes no reference to the physical constitution of matter an atomic theory is an abuse of language. Consequently, with such a theory, be its intrinsic merits or demerits what they may, chemists will be chary of associating Dalton's name. A theory which is not even atomic, cannot be the Daltonian theory.

Dalton was a leader of scientific thought regarding the constitution of matter. There is no reason to think that he so much as dreamed of a distinction between the chemical and physical constitution of matter. If this were the place to consider the genesis of Dalton's theory, it could be shown that the general doctrine that matter is made up of atoms was applied by Dalton to the consideration first of purely physical phenomena. From this as a starting point he was led to the consideration of chemical phenomena. Once formed, his theory was not an exclusively chemical one. Dalton offered to explain the structure of matter, taking into account both chemical and physical properties. Thus, after adducing chemical evidence that "no two elastic fluids, probably, . . . have the same number of particles, either in the same volume or the same weight," Dalton goes on to show that "the quantity of heat belonging to the ultimate particles of all elastic fluids must be the same under the same pressure and temperature."[1]

The structure of matter, and the chemical changes which it undergoes, Dalton explains in terms of atoms. In his mind's eye he analysed all matter into compound or simple atoms of different kinds, and these compound atoms finally into simple atoms which could not be analysed further. These simple atoms are the basis of his system.

One of the great characteristics of Dalton's atom was that it could not be split. In Henry's "Memoirs of Dalton," an account is given of a conversation with Dalton that shows how much his mind dwelt on this idea. Dalton "concluded with a few remarks on the ternary compounds, and alluded to the peroxide of hydrogen as one;[1] pointing out *that in these the principle of* MULTIPLE PROPORTION *existed*, for, as he said with great naïveté, 'thou knows IT MUST BE SO, *for no man can split an atom.*' I ventured, however, to allude to the sesquioxides, but was at once silenced by his answer, 'Yes, but THEY are 3 atoms to 2.'"[2]

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[1] A. C. R., 4, 5-6.

Dalton was the pioneer of a scientific atomic theory; beyond doubt, ever since he made known his theory, chemists have made constant use of the word "atom." It does not therefore follow that the atomic theory is due solely to Dalton; the word "atom" did not originate with him. Even more important than the word is what the word means. To the adherents of the kinetic theory of gases it means one thing, it meant another thing to Dalton, and yet another to Lucretius.

It is unfortunate that the words atom and molecule are used sometimes as meaning the same thing. The chemist recognises the existence of the molecule of oxygen and also of the atom. This distinction between the atom and the molecule being established, it is not only convenient, but imperative, to mark the distinction, by using the two words in different ways.

Given the idea of the chemical elements, what is the difference between the way in which they are regarded by modern chemists and by Dalton? The modern chemist recognises atoms of two orders; he analyses the elements into "molecules," and then the "molecules" into "atoms." The picture in Dalton's mind was not quite the same; for him, the elements consisted of but one order of particles. The question then arises, is Dalton's atom the same in idea as the modern molecule or the modern atom?

The answers to this question are usually more dogmatic than reasonable. The question is decided off-hand, as if no other answer were possible than the particular one given. Ostwald holds that Dalton's atom is the modern atom. Divers states that "Dalton's atoms were both the atoms and the molecules of present-day chemistry, but much more the latter than the former." These are so many confessions of faith, which afford no ground of reasonable belief. Moreover, there is evidently need as well as scope for a careful examination of the question, inasmuch as the conviction of Ostwald is at variance with the conviction of Divers.

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[1] $H=1$ and $O=8$, so that water, OH, was a binary compound, and hydrogen peroxide, HO_2, a ternary compound.

[2] Henry, p. 222.

The modern atom is a subordinate idea, inasmuch as it is based on the idea of the molecule. Our knowledge of atomic oxygen is almost entirely derived from our knowledge of the different molecules which contain oxygen; we have almost no knowledge of oxygen in the state of free atoms. Dalton's atom was an independent and not a subordinate idea. His conception of the atom could give him no insight into the modern atom as dependent on the molecule. Of oxygen in the atomic state, different as it is from molecular oxygen, Dalton had no notion whatever.

This much more there is in common between Dalton's atom and the modern molecule, that the two are the units of chemical action. Water is formed according to the modern chemist from molecules of hydrogen and oxygen, from atoms of hydrogen and oxygen according to Dalton.

In one important respect the two conceptions differ, namely, that Dalton's atoms were indivisible, whereas the modern molecule may be split. According to Dalton, one atom of oxygen could form not more than one compound atom of water. The modern molecule of oxygen, yielding with hydrogen two molecules of water, is divided into two parts. To this conception of a molecule of oxygen divisible into two parts, Dalton would have given short shrift. His devotion to his own conception was perfect; he said, "No man can split an atom." In this respect Dalton's atom and the modern atom are much the same, the modern atom being something that has not been split. Here a qualification is needed. The modern atom is a more pliable conception than Dalton's, and means simply the limit of the division of ordinary matter.[1]

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[1] v. chapter V., pp. 29-30.

Divers asserts that "Dalton distinctly guarded himself against being understood to claim for the atom more than chemical indivisibility" Divers, p. 5. This, without quotation of Dalton's words, or even of the reference.

Having communicated with Dr. Divers, I do not understand him, in his reply, to show any intention of maintaining the above position.

The result of the inquiry is, that Dalton's atom, in being indivisible, is like the modern atom, and like the modern molecule in being an independent conception, and in being the unit of chemical action.

In this connection I must mention a phrase of Divers' which can no longer be allowed to pass without challenge. Divers says:—"Dalton gave us the conception of the molecule though confused with the idea of the atom."[1] In science, *confused* is nothing if not a term of reproach. It is a strange word to use in speaking of the conceptions of a logical intellect like Dalton's, above all, a strange word in the mouth of a critic who decides that the "modern theory of chemistry is indisputably the atomic theory of Dalton." Any theory which is based on a confused idea, must, I submit, be a confused theory.

At the point of view from which I suggest that Dalton's atom should be looked at, there is no need to call it a confused idea. Surely it was a unique idea; it was something that could not be split, and that was the unit of chemical action. Combining ideas that we now keep separate, Dalton's atom is partly like the modern atom and partly like the modern molecule. In general, it is impossible to say that the Daltonian atom of an element is either the modern atom or molecule of that element. There are, nevertheless, at the present day certain elements whose molecules realise Dalton's conception. All molecules which have never been divided do this; for instance, the molecule of mercury. However, the monatomic molecule, while it satisfies his conception of the atom, is a special case.

Dalton used the word atom in connection with elements and also compounds. On this point, which will be taken up later, I may for the present simply quote his own words:—"I have chosen the word *atom* to signify these ultimate particles, in preference to *particle*, *molecule*, or any other diminutive term, because I conceive it is much more expressive; it includes in itself the notion of *indivisible*, which the other terms do not. It may perhaps be said that I extend the application of it too far, when I speak of *compound*

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[1] Divers pp. 8-9.

atoms; for instance, I call an ultimate particle of *carbonic acid* a *compound atom.* Now, though this atom may be divided, yet it ceases to be carbonic acid, being resolved by such division into charcoal and oxygen. Hence I conceive there is no inconsistency in speaking of compound atoms, and that my meaning cannot be misunderstood."[1]

Assuming the combination of atoms in definite proportions, Dalton is able to explain the laws of multiple and reciprocal proportions. The atoms are the units of chemical action; between simple atoms, chemical action gives rise to compound atoms. Two different atoms combining with one another, numerous repetitions of this event yield a finite amount of a particular substance. A second substance may arise by the union of an atom of one kind with two of another. Dalton expresses himself as follows:—"If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple, namely:—

1 atom of A + 1 atom of B = 1 atom of C, binary.
1 atom of A + 2 atoms of B = 1 atom of D, ternary.
2 atoms of A + 1 atom of B = 1 atom of E, ternary.
1 atom of A + 3 atoms of B = 1 atom of F, quaternary.
Etc., Etc."

In arriving at the formulæ of compounds, Dalton made use of a set of rules, and it is these rules which form the arbitrary features of his system. They are as follows:—

"The following general rules may be adopted as guides in all our investigations respecting chemical synthesis.

"1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary.

"2nd. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.

"3rd. When three combinations are obtained, we may expect one to be a *binary* and the other two *ternary*.

"4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, etc.

"5th. A *binary* compound should always be specifically heavier than the mere mixture of its two ingredients.

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[1] New View of Dalton's Atomic Theory, Roscoe and Harden, 1896, pp. 111-2.

"6th. A *ternary* compound should be specifically heavier than the mixture of a binary and a simple, which would, if combined, constitute it; etc."

It may be pointed out now how these rules justify Dalton's extension of the word atom to compound substances. His seventh and last rule is:—"The above rules and observations equally apply, when two bodies, such as C and D, D and E, etc., are combined."[1] Thus the compound atom C, *on reacting chemically with another atom, did not undergo division.*

1 atom of C + 1 atom of D = 1 atom of G.

In Dalton's mind, therefore, chemical combination was essentially additive, and not of the nature of double decomposition.

Divers, inasmuch as he declares that "the theory of chemistry, with all its modern developments, is indisputably the theory of Dalton," may justly be held responsible for any want of conformity between his own account of the modern theory, and Dalton's theory. Divers maintains that chemical change is essentially a matter of double decomposition, two molecules on reaction yielding two molecules. Dalton regarded chemical combination as addition, pure and simple, two atoms on combination yielding one.

On the above rules two remarks may be made. In the first place, the rules are in accordance with the laws of chemical combination by weight, so that Dalton's theory is adapted to express the gravimetric composition of matter.

Second, except in rules 5 and 6, there is no reference to the composition of matter by volume. On this topic Dalton's views will now be considered.

Dalton's theory, on his own showing, was incompatible with what we know as Avogadro's hypothesis. It is easy to prove this. It is much less easy to understand why chemists should give accounts of Dalton's theory which pass over this incompatibility as a thing of no importance.

In the course of his reflections upon atoms, Dalton undoubtedly took Avogadro's hypothesis into consideration. His own account of the matter is to be found in the "New

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[1] A. C. R., 2, 30.

System of Chemical Philosophy." "At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous; or if not, that we had no data from which the question could be solved. But . . . I became convinced that different gases have *not* their particles of the same size."[1]

The essay on "The Constitution of Mixed Gases" was read in 1801, the "New System of Chemical Philosophy" was published in 1808, and Avogadro's paper in 1811. Between 1801 and 1808, therefore, Dalton took into consideration and rejected as untenable the very hypothesis which Avogadro espoused in 1811.

The ground of this objection is given by Dalton as follows:—"It is evident the number of ultimate particles or molecules in a given weight or volume of one gas is not the same as in another; for, if equal measures of azotic and oxygenous gases were mixed, and could be instantly united chemically, they would form nearly two measures of nitrous gas, having the same weight as the two original measures; but the number of ultimate particles could at most be one-half of that before the union. No two elastic fluids, probably, therefore, have the same number of particles, either in the same volume or the same weight."[2]

In view of the repudiation of Avogadro's hypothesis in 1808, contained in Dalton's exposition of the atomic theory, there would seem to be little ground for the supposition that in the structure of the theory Dalton made any use of the hypothesis. Notwithstanding, Debus maintains the contrary, and goes so far as to say that by 1810 Dalton had reconsidered the matter and accepted the hypothesis. Here I am very little concerned about the question if Dalton made any use of the hypothesis during the early days of the theory. For the purposes of this essay the important thing is to find out if there are any grounds for the supposition that by 1810 Dalton had solved the objections, and abandoned the conviction of 1808.

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[1] A. C. R., 4, 6-7. [2] A. C. R., 4, 5.

Debus denotes Avogadro's hypothesis by the symbol M/S = C. His case is as follows. He first quotes Dalton's maxim, namely, "*That every species of pure elastic fluid has its particles globular and all of a size; but that no two species agree in the size of their particles*, the pressure and temperature being the same." Debus then proceeds:—"So Dalton wrote in the first part of his work, which was published early in the year 1808. In the second part, the preface to which was written in November, 1810, the atomic composition of the oxides of nitrogen and of carbon is determined by means of the hypothesis M/S = C, and on p. 560 five gases are specified, which have absolutely the same molecular volume.[1] Thus Dalton must have found cause, subsequent to the year 1808, to abandon his maxim."[2]

In saying that Dalton determined the atomic composition of the oxides of carbon by means of the hypothesis M/S = C, what Debus means is, that Dalton, knowing that carbon dioxide is the heavier of the two oxides, inferred that it was the more complex compound. Debus remarks:—"Thus the composition of carbon dioxide was given by the formula CO_2, of carbon monoxide by the formula CO. Such a conclusion can be derived from the specific gravity of gases only if equal volumes of the gases contain the same number of molecules."[3]

I should have thought it quite possible that Dalton derived the composition of the two oxides of carbon as above, without believing in the M/S = C hypothesis, but Debus does not think so. However, there are two objections to Debus' opinion. The first objection is, that the evidence is indirect. Debus adduces only circumstantial evidence as to Dalton's belief. The case amounts to this, that in certain passages of the "New System" of 1810, a belief in the $M/S = C$ hypothesis is implied. Debus cannot maintain that in 1810 Dalton said, "I now believe in this hypothesis." I think Dalton, if he had come by then to believe in the hypothesis, would have said so.

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[1] Of the different gases known to Dalton in 1810, five, it seems, had exactly the same molecular volume, so that presumably, all the other gases had different molecular volumes. Hydrogen, he thought, had about twice the molecular volume of oxygen. v. p. 65.

[2] So schrieb Dalton im ersten Teile seines Werkes, der im Frühjahr 1808, herauskam. Im zweiten Teile, dessen Vorrede im November 1810 geschrieben ist, wird die atomistische Zusammensetzung der Oxyde des Stickstoffs und des Kohlenstoffs mittels der Hypothese M/S = C bestimmt. Und auf S. 560 werden fünf Gase aufgeführt, die absolut gleiches Molecularvolumen besitzen. Dalton muss also nach dem Jahre 1808 Gründe entdeckt haben, welche die Aufhebung seiner Maxime veranlassten. Zeitschrift, 20, 285.

[3] Die Kohlensäure wäre also nach der Formel CO_2, das Kohlenoxyd nach der Formel CO zusammengesetzt. Ein solcher Schluss lässt sich nur dann aus den spezifischen Gewichten der Gase ableiten, wenn in gleichen Volumen derselben eine gleiche Anzahl von Molekeln enthalten ist. Zeitschrift, 24, 335.

The second objection is that Debus' opinion is very hard to reconcile with Dalton's attitude towards Gay-Lussac's law.

The law was published in 1809. In 1810, in the "New System," Dalton makes strictures on the law, and comes to the following conclusion:—"The truth is, I believe, that gases do not unite in equal or exact measures in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments. In no case, perhaps, is there a nearer approach to mathematical exactness, than in that of one measure of oxygen to two of hydrogen; but here, the most exact experiments I have ever made gave 1·97 hydrogen to 1 oxygen."[1]

Among chemists, the firmness of Dalton's antipathy to Gay-Lussac's law is not enough known. Tilden says, "Gay-Lussac's facts have always been admitted, except for a time by Dalton."[2] Reference is made to the law in volume 2, part 1, of the "New System," published in 1827. Dalton mentions the "combination of gases in equal volumes, and in multiple volumes. . . . The cases of this kind, or at least approximations to them, frequently occur; but no principle has yet been suggested to account for the phenomena; till that is done I think we ought to investigate the facts with great care, and not suffer ourselves to be led to adopt these analogies *till some reason can be discovered for them*."[3] How unwilling Dalton was to admit the truth of Gay-Lussac's law, these words show. If they imply an admission, no admission could well be more grudging or more guarded.

Debus gives an explanation of his own of this rooted antipathy to Gay-Lussac's law. He points out that in Dalton's system water was OH, nitric oxide NO, and ammonia NH. Then, retaining the formulæ OH and NO, and granting Gay-Lussac's statement that ammonia consists of 1 volume of nitrogen to 3 volumes of hydrogen, Debus goes through a train of argument to show that ammonia is N_2H_3. "For the composition of ammonia, Dalton's principles bespoke one atom of each element. There is a contradiction here. Dalton had to choose between Gay-Lussac's law of volumes and his atomic theory, . . . he threw over Gay-Lussac's law."[1]

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[1] A. C. R., 4, 27. [2] Short History, p. 62. [3] Henry, p. 172.

Among the objections that Dalton does adduce to Gay-Lussac's law, I find no sign of the train of thought given in all detail by Debus. Even if the argument in itself be above suspicion, there is the objection to it, that it is quite unauthentic, and seems to have originated entirely with Debus. Yet, comparatively, this is a matter of slight importance. The fact is, and this is the important thing, that Debus holds that at one and the same time Dalton could be a believer in Avogadro's hypothesis and not in Gay-Lussac's law. Given the law of constant proportions, everybody, with the exception of Debus, recognises that Gay-Lussac's law is a necessary consequence of Avogadro's hypothesis. Consequently, I can only suppose that the hypothesis is understood by Debus in some esoteric sense, and to him does not mean what it does to other people.

In contrast to Debus, Dalton recognised that the association between the hypothesis and the law is of the closest kind; in fact, he regarded them as tantamount to one another. I can only regard Debus' supposition that Dalton believed in Avogadro's hypothesis in 1810 as improbable in the extreme, inasmuch as Dalton, while rejecting Gay-Lussac's law, identified the law with the hypothesis. In 1810, in the course of his strictures on the law, he refers to his repudiation of the hypothesis in 1808:—"Gay-Lussac could not but see that a similar hypothesis had been entertained by me, and abandoned as untenable; however, as he has revived the notion, I shall make a few observations upon it, though I do not doubt but he will soon see its inaccuracy." And again, Gay-Lussac's "notion of measures is analogous to mine of atoms; and if it could be proved that all elastic fluids have the same number of atoms in the same volume, or numbers that are as 1, 2, 3, etc., the two hypotheses would be the same, except that mine is universal, and his applies only to elastic fluids."[1]

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[1] Dalton's Grundsätze verlangen für Ammoniak ein Atom von jedem Element. Hier ist ein Widerspruch. Dalton hatte also die Wahl zwischen Gay-Lussacs Volumengesetz und seiner Atomtheorie . . . so verwarf er Gay-Lussacs Volumengesetz. Zeitschrift, 20, 375-6.

Dalton's proceeding, in rejecting Avogadro's hypothesis and Gay-Lussac's law alike, fixes the character of his theory. It was a theory primarily and almost exclusively of the composition of matter by weight. ✓

Clerk Maxwell also identified Gay-Lussac's law and Avogadro's hypothesis. He first states the proposition that "If equal volumes of two gases are at the same temperature and pressure . . . the masses of the two kinds of molecules are in the same ratio as the densities of the gases to which they belong." He then goes on to say that "this statement has been believed by chemists since the time of Gay-Lussac."[2] I take this to mean that it had never occurred to Maxwell that anyone could believe in Gay-Lussac's law and not in Avogadro's hypothesis. Dalton was of much the same mind as Maxwell; he was "for thorough," and rejected hypothesis and law together. However, for long chemists were of a different mind. The consequences of rejecting Avogadro's hypothesis and at the same time accepting Gay-Lussac's law will be seen in the two following chapters.

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[1] A. R. C., 4, 25.

[2] E. B., Article Atom.

CHAPTER X.

THE ATOMIC WEIGHT SYSTEMS OF BERZELIUS.

> *We meet with truths overstated or misdirected, matters of detail variously taken, facts incompletely proved or applied, and rules inconsistently urged or discordantly interpreted. Such, indeed, is the state of every deep philosophy in its first stages.*—NEWMAN.

In the investigation of atomic weights, there are two distinct problems to be solved—(1) the determination of experimental data, (2) the interpretation of the data by a formula showing the relative number of atoms in the molecule. It is the second only of these problems which is considered here.

Berzelius was the earliest of the great masters of atomic weight determination. Wide in its scope, his work included the analysis of compounds of all the elements then known; his data were the most accurate of his day. Berzelius published two systems of chemical formulæ, the later of which came into extensive use among chemists. He adhered to his first system from about 1810 to 1820. To the second system, which was published in 1826, he adhered till the end of his life.

The compounds of sulphur received the same formulæ in both systems. Berzelius recognised four oxides of sulphur, namely, the respective anhydrides of thiosulphuric, sulphurous, dithionic and sulphuric acids. These were SO, SO_2, S_2O_5, SO_3.

The essential differences between the two systems are involved in the formulæ which Berzelius assigned to the compounds of the metals and of nitrogen. The elements generally were supposed in the earlier system to enter into their compounds with oxygen chiefly one atom at a time, metals and non-metals alike. There results, says Berzelius, "a much greater simplicity in the composition of substances, and the number of simple atoms, required for the production of every compound atom, becomes much less when, for example, I suppose that sulphurous acid, ferrous oxide, sodium oxide are RO_2, and sulphuric acid, ferric oxide, and sodium peroxide RO_3, than when I consider them as RO and R_2O_3."[1]

Accordingly, the formula for nitric anhydride was NO_5, so that O being 16, N was 28. In the 1826 system the objections to such a formula as R_2O_3 were abandoned. For the oxides of nitrogen, Berzelius arrived at the formulæ N_2O, NO, N_2O_3,[2] N_2O_5. Thus nitrogen, unlike sulphur, enters into its compounds chiefly two atoms at a time.

In 1826 Berzelius had to decide whether the oxides of the metals belonged to the nitrogen or the sulphur series of oxides. Here a great difference arose between the two systems. In the earlier system there was but one series, the sulphur series, recognised, and the oxides of a metal were supposed to contain each one atom of the metal. In the later system the nitrogen series was adopted, metallic oxides being each supposed to contain two atoms of the metal.[3] As regards atomic weights, this means that in the earlier system the atomic weights of the metals are double what they are in the later system. Thus chromic oxide was first CrO_3, and then Cr_2O_3, and chromic anhydride was first CrO_6, and then Cr_2O_6 or CrO_3. Taking O = 16, the earlier formulæ involve for chromium the value 104, and the later formulæ the value 52.

The historians of chemistry have often remarked how close the chemical formulæ of this later system come to those of the present day. In this respect, Gmelin's system, which came into competition with that of Berzelius, shows at a disadvantage. For water and nitric oxide respectively, Gmelin gives the formulæ HO and NO_2, Berzelius H_2O and NO.

Much more important than formulæ are the principles on which formulæ are arrived at. The formulæ of Berzelius being so nearly those of to-day, his principles are all the more interesting. Criticism of them must determine two things—(1) How far the principles were consistent with one another, (2) what there is in common between them and those on which chemical formulæ are arrived at to-day. In particular, since Dulong and Petit's law was published in 1819, and Mitscherlich's law in 1821, it is of special importance to note in the construction of the system of 1826 what use Berzelius made of these laws.

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[1] There results "une plus grande simplicité dans la composition des corps, et le nombre des atomes simples, nécessaire pour la production de tout atome composé, devint beaucoup moindre, quand je supposai, par exemple, que l'acide sulfureux, l'oxidule de fer, la soude, etaient RO_2, et l'acide sulfurique, l'oxide de fer et le superoxide de sodium RO_3, que lorsque je les considérais comme RO et R_2O_3." Essai, 1819, pp. xiv.-xv.

[2] Berzelius believed then that the oxide NO_2 did not exist.

[3] However, all strong bases received the general formula RO. For the explanation of this, see p. 73.

The guiding principles of the system of 1826, as given by Berzelius, are four in number.[1] They are:—

(1) Consideration of the series of oxides (or sulphides) formed by an element. When an element forms two oxides, in which, for a given amount of the element, the amounts of oxygen are in the ratio 1 : 2, the formulæ of the oxides are XO and XO_2, or XO_2 and XO_4; the ratio being 2 : 3, the formulæ are XO and X_2O_3; the ratio being 3 : 4, the formulæ are X_2O_3 and XO_2; the ratio being 3 : 5, the formulæ are X_2O_3 and X_2O_5, or XO_3 and XO_5.

(2) In the formation of a salt, consideration of the ratio (oxygen in electro-negative oxide) : (oxygen in electro-positive oxide). When the two oxides combine, the oxygen of the negative oxide is a multiple by a whole number of the oxygen of the positive oxide; at the same time this number, as a rule, is the number of atoms of oxygen in the negative oxide.

(3) Mitscherlich's law of isomorphism. According to this law, similar formulæ are ascribed to isomorphous substances.

(4) The principle based on the volume theory of Berzelius. This theory, which was suggested by Gay-Lussac's law concerning the combining volumes of gases, is that equal volumes of different gaseous elements contain the same number of atoms.

Of these four methods the first and second are common to both systems, and the third belongs to the later system only. In the earlier system the fourth method, based on the volume theory, had been enunciated, but not developed. There, the sole instance of its use is in the determination of the formula of water and at the same time of the atomic weight of hydrogen. The atomic weight of nitrogen in the earlier system is not in accordance with the volume theory. For nitric anhydride the formula was NO_6, while the volume theory leads to the formula N_2O_5.

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[1] Pogg. Ann., 1826, 7, 397; 8, 1,177.

Berzelius did not give the same weight to each of the four methods used in the 1826 system. Only method 4, based on the volume theory, gives results which are quite free from uncertainty.[1]

As for isomorphism, Berzelius states that aluminium, ferric and manganic oxides are isomorphous, that ferrous, manganous, cupric, cobalt, nickel, zinc, magnesium, and calcium oxides are isomorphous, and that calcium, strontium, and barium oxides are isomorphous. "For obvious reasons, this relation gives just as positive results as the measurement of the relative volume of the constituents in the gaseous state." This statement, of course, is to be taken with the qualification that the method can be used only in subordination to other methods. "If the number of atoms in a single one of these eleven oxides can be determined with certainty, it is known for them all."[2]

Ladenburg states that the volume theory "can only be used to determine the relative number of atoms in a very few compounds, and the founder of the first chemical system is therefore obliged to seek for other generalisations of more universal validity."[3] With this verdict I am not at all satisfied. In the earlier system, Berzelius did not make use of the volume theory to its full extent. In the 1826 system he succeeded in making a very extensive use of it. In the first place, by the use of the theory he arrived at the atomic weights, relative to oxygen, of hydrogen, nitrogen, and chlorine, and at the formulæ of their compounds with one another. In the second place, in arriving at the atomic weights of the remaining elements, Berzelius was continually drawing analogies between their compounds and those of hydrogen, nitrogen, and chlorine. Chloric anhydride being Cl_2O_5, bromic and iodic anhydrides are Br_2O_5 and I_2O_5 respectively. For the anhydride of dithionic acid a weighty reason in 1826 for adopting the formula S_2O_5 in preference to S_4O_{10}, was that S_2O_5 is analogous to Cl_2O_5 and N_2O_5.

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[1] "Eine einzige derselben giebt Resultate, welche keinem Zweifel unterworfen sind, die nämlich, wo man die relativen Volume, nach welchen sich die Bestandtheile eines Körpers verbinden, in Gasform bestimmen kann." Pogg. Ann., 7, 399.

[2] "Aus leicht einzusehenden Gründen kann dieses Verhältniss eben so positive Resultate geben, als die Messung der relativen Volume der Bestandtheile in Gasform. . . . Wenn die Anzahl von Atomen in einem einzigen dieser 11 Oxyde mit Sicherheit bestimmt werden kann, sie für alle bekannt ist." Pogg. Ann., 7, 403.

[3] Ladenburg, p. 93.

It is easy to show that Berzelius placed much reliance on method 4, and was well aware how inconclusive are methods 1 and 2. Consider the oxides of phosphorus, for example: they may be either PO_2, PO_3, PO_5 (a), or PO, P_2O_3, P_2O_5 (b). Method 1 cannot decide between these alternative sets of formulæ. A decision was come to only on appeal to other considerations.

Regarding method 2 as inconclusive, Berzelius rejects it. Phosphoric acid received the formula P_2O_5 in opposition to method 2. In the case of nitric, chloric, iodic, and dithionic anhydrides the ratio (O in anhydride) : (O in equivalent amount of base) is 5 : 1. In the case of phosphoric acid the ratio is 5 : 3.

Method 3 is also ignored. Phosphoric acid is not isomorphous with chloric, nitric, iodic, nor dithionic acid. Berzelius adopts the formula P_2O_5, because he thinks that phosphoric anhydride containing five atoms of oxygen is analogous after all to these other anhydrides, and also because then phosphine and ammonia, which Berzelius knew to be analogous substances, received similar formulæ. Inasmuch as in all this he is relying on analogies with substances of known formulæ, it is clear that Berzelius gives the ascendency to the method by which these formulæ are decided, that is, to the volume theory.

It is now time to consider what there is in common between the principles of Berzelius and those of to-day. The subordinate method of isomorphism is common to both. Methods 1 and 2 can hardly be regarded now as atomic weight methods at all, 1 being very often inconclusive, and 2 sometimes right and sometimes wrong. Berzelius did not always accept the evidence of method 2, and when he did accept it, he was more than once misled. Thus he was led to the formula BO_3 for boric anhydride and SiO_3 for silicic anhydride.

Consideration in full of method 4 being reserved for the next chapter, there remains to be considered in this section what use Berzelius made of Dulong and Petit's law. He had classified the oxides of the metals by laying down a series of typical oxides, and, alongside of this, alternative series of formulæ, the sulphur series and the nitrogen series.

1. Cuprous oxide	RO	R_2O
2. Cupric and ferrous oxides, etc.	RO_2	RO
3. Ferric and manganic oxides, lead sesquioxide, etc.	RO_3	R_2O_3
4. Lead and manganese peroxides	RO_4	RO_2
5. (Manganic anhydride, *sic*)	RO_6	R_2O_6

In the earlier system Berzelius interpreted the data by the formulæ RO, RO_2, etc., that is, the sulphur series; in the later system, by the formulæ R_2O, RO, etc., that is, the nitrogen series. This resulted in all strong bases receiving the general formulæ RO in the later system, because, lead and calcium carbonates being isomorphous, and lead oxide being PbO, calcium oxide was CaO. Hence sodium oxide was NaO, and silver oxide AgO.

In order to understand the use that Berzelius made of Dulong and Petit's law, it is necessary to examine into his reasons, in 1826, for referring the oxides of the metals to the nitrogen series. The reasons[1] are as follows:—

1. The sulphur series involves formulæ with a large number of oxygen atoms, and at the same time, suggests that there exist many more oxides of the metals than are known. For chromic anhydride the formula CrO_6 suggests that the oxides of chromium are more numerous than they are found to be, hence the formula CrO_3 is preferable.

2. For cuprous oxide Cu_2O is more likely to be right than CuO, because the oxide readily yields cupric oxide and copper. Similarly, mercurous oxide is Hg_2O.

3. Taking the nitrogen series of formulæ, Dulong and Petit's law holds for sulphur, gold, platinum, tin, bismuth,[2] copper, lead, zinc, nickel, and iron.

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[1] Pogg. Ann., 7, 412 et seq.

[2] Later on, bismuth fell out of this list. Berzelius gave bismuthous oxide the formula Bi_2O_3, in 1826, and about 1835 saw fit to change this to BiO.

4. The oxides of chromium may be CrO and CrO_3, more probably they are Cr_2O_3 and CrO_3, for two reasons. For one, chromic oxide is isomorphous with ferric and manganic oxides, which are probably Fe_2O_3 and Mn_2O_3. For another, the ratio (O in chromic anhydride) : (O in equivalent amount of base) is 3 : 1.

Further, Berzelius explicitly says that the choice of the nitrogen series of oxides as types of the metallic oxides was above all determined by consideration of chromium and manganese compounds. "I freely admit that the relations of chromium and manganese, above all others, determined me to fix on the nitrogen series as the most correct, according to all probability."[1]

As to this decision between the sulphur and the nitrogen series for the oxides of the metals, in favour of the nitrogen series, Ladenburg remarks, "He rejects the apparently most natural assumption of one atom of radical, which he had made in 1819, since it leads him to atomic weights that are not in harmony with Dulong and Petit's law."[2]

Here Ladenburg gives a wrong impression by taking no account of the other reasons for the change. For one thing, he overlooks the fundamental fact that but for the volume theory, Berzelius would have had only the sulphur series to adhere to. In adopting the formulæ N_2O, NO, N_2O_3, N_2O_5 for the oxides of nitrogen, Berzelius was fulfilling the requirements of the volume theory.

Having given the list of ten elements (see p. 73) which can be brought into accordance with Dulong and Petit's law, Berzelius remarks, "a convincing reason, if one assumes that the atomic weight of sulphur is known, for halving the atomic weights of the others."[3] These words support Ladenburg, considered apart from their context and the drift of Berzelius' meaning, but not otherwise.

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[1] "Ich bekenne aufrichtig, dass die Verhältnisse des Chroms und Mangans, vor allen andern, mich bestimmt haben, die Reihe des Stickstoffs, als die, allen Wahrscheinlichkeit nach, richtigste zu wahlen." Pogg. Ann., 7, 416.

[2] Ladenburg, p. 99.

[3] "Ein überzeugender Grund, um, wenn man das Atomgewicht des Schwefels als gekannt annimmt, das der übrigen zur Hälfte herabzusetzen." Pogg. Ann., 7, 413.

It is significant that Berzelius does not put Dulong and Petit's law among his principal atomic weight methods. He draws attention to the need for further work upon the relation between specific heat and atomic weight. Silver, tellurium, arsenic, antimony, and cobalt he recognised as being exceptions to the law. Silver is exceptional, because silver oxide got the formula AgO. The other exceptions were due to errors in the specific heat data.

Ladenburg appears to have overlooked the passage in which Berzelius mentions the compounds of manganese and chromium as having determined him to fix on the nitrogen series as types of the metallic oxides. This passage only appears to be in contradiction to the one about Dulong and Petit's law.

Berzelius' meaning is, I take it, that among the four different reasons that he adduces for the change in question, it was Dulong and Petit's law that turned the scale. Undoubtedly, there being other three reasons for the change, he was not going to forego the additional advantage of Dulong and Petit's law.

Taking this view of the matter, and remembering that Berzelius accepted Dulong and Petit's law with reserve, and that the law is not given among his principal atomic weight methods, I conclude that this law was at most a minor consideration with him.

Reviewing Berzelius' atomic weight methods, one need have little hesitation in deciding that he gave most weight by far to the volume theory. On that theory he arrived at the atomic weights relative to oxygen, of hydrogen, nitrogen, and chlorine. In deciding on the atomic weights of the generality of the elements he was continually abandoning the other methods and referring compounds to the compounds of nitrogen and chlorine. By reference to chlorine he satisfied himself as to the atomic weights of bromine and iodine, and, as another instance, by reference to nitrogen he satisfied himself as to the atomic weights of phosphorus and arsenic. I therefore conclude that the keystone of the system of 1826 was the volume theory.

CHAPTER XI.

THE ATOMIC WEIGHT SYSTEM OF GMELIN.

About the year 1840, Berzelius' system of chemistry found itself threatened by the rivalry of Gmelin's system. This system, first made known previous to 1820, can be considered here only as it was expounded in Gmelin's "Handbuch der Chemie," in 1843.

In Ladenburg's "History of Chemistry," I find the following description of the situation in the chemical world about the year 1840:—"A new school had arisen . . . which sought, successfully, to supplant the system of Berzelius. At the head of this movement there stands L. Gmelin." As to the *raison d'être* of this movement, Ladenburg says, "It had come to this, then—inorganic chemistry, in conjunction with physics, had not been able to maintain the conception of the atom." "At the end of the fourth decade of this century, we find the atomic theory—the most brilliant theoretical achievement of chemistry—abandoned and discredited by the majority of chemists, as a generalisation of too hypothetical a character."[1]

This account of the school of Gmelin I am quite unable to accept. It may be quite true that some chemists of that school were doubters in regard to the atomic theory. It is quite true that Gmelin began as a doubter, and this is all that Ladenburg proves by the reference which he gives to Gmelin's "Handbuch der Theoretischen Chemie," 2nd edition, of the date 1821. Ladenburg seems quite unaware that by 1843 Gmelin had come to be a believer in the atomic theory.

In the "Handbuch" of 1843, translated into English by Watts in 1848, the school opposed to the atomic theory is mentioned by Gmelin in the impartial way:—"The relative weight . . . by those who either reject the atomic theory altogether, or regard it as not sufficiently established, is called the *combining weight, chemical weight, chemical equivalent, combining proportion, equivalent proportion, or equivalent number, stoichiometrical proportion, or stoichiometrical number.*"

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[1] Ladenburg, pp. 106-7.

Gmelin's account[1] of the atomic theory is not given out of a sense of duty and for the sake of completeness, much less from the standpoint of an opponent. He speaks as follows of the laws of combination in multiple and reciprocal proportions:—"The origin of these two laws is most satisfactorily explained by the atomic theory, . . . according to which every simple substance consists of very small indivisible particles called *atoms*, these atoms being of uniform weight and volume in each individual substance, while the atoms of different substances may be of different weight and volume." Again, "to every simple substance there belongs a certain relative weight," which, "by those who admit the atomic theory, is called the *atomic weight*." Gmelin was one of these, and he gives a table which is headed, "Atomic Weights of the Elementary Bodies."

The reason for the change from Berzelius' system to Gmelin's cannot be what Ladenburg alleges. It is simply a mistake to suppose that Berzelius and Gmelin were at variance on the fundamental question of the constitution of matter. Both believers in the atomic theory, they differed in regard to particular principles. I shall show that Berzelius' characteristic principle, the volume theory, had become untenable, and that Gmelin, believing in the atomic theory, adhered to Dalton's conception of the atom, in opposition to a departure from that conception made by Berzelius in order to save his volume theory.

In arriving at atomic weights, Gmelin made use of six principles. First of all, I shall give four principles on which Gmelin and Berzelius were at one. They are as follows:—

(1) "As a general rule, the total weight of the atoms composing an acid must be of such amount that the compound atom may just suffice for the saturation of one atom of a salifiable base. Thus 16 sulphur and 3 × 8 oxygen form 40 sulphuric acid, and 103·8 lead with 8 oxygen form 111·8 oxide

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[1] Gmelin, 1, 42-50.

of lead: now 40 sulphuric acid just satisfy 111·8 oxide of lead . . . To this rule there are, however, certain unmistakable exceptions . . ."

(2) "When a metal combines with oxygen in one proportion only, to form a salifiable base, it is assumed, supposing that the laws of isomorphism do not oppose the assumption, that the compound contains equal numbers of atoms of the metal and of oxygen." Thus potash was KO. "When a metal forms a number of salifiable bases with different proportions of oxygen, the oxide which forms the strongest base is to be regarded as containing the metal and oxygen in equal numbers of atoms." Accordingly, ferrous oxide was FeO, mercuric oxide HgO, cupric oxide CuO, and stannous oxide SnO.

(3) "It is supposed that substances which closely resemble one another in physical and chemical properties, combine with a third body, according to the same number of atoms. If nickel combines with oxygen in the proportion of 1 : 1 and 2 : 3 At., this must also be the case with cobalt, which bears so very closely an analogy to nickel."

(4) Isomorphism. The one oxide of aluminium, but for the isomorphism with ferric oxide, would be AlO. Ferric oxide being Fe_2O_3, the other is Al_2O_3.

These four methods, substantially, are given by Berzelius also. The methods put into use, the only important differences that arose are in regard to bismuth and silicon. To silica Gmelin gave the formula SiO_2, Berzelius SiO_3. To bismuthous oxide Gmelin gave the formula Bi_2O_3, Berzelius BiO.

The great difference between the two chemists depends upon the two remaining principles of Gmelin, both of which are at variance with the volume theory of Berzelius. This theory had been for some time under a cloud. By work which began in 1826, Dumas showed that the theory did not hold in the cases of mercury, phosphorus and sulphur. In 1834 Mitschlerlich confirmed these results, and added arsenic to the list of exceptions. According to the volume theory, atoms of the elements occupy equal volumes. What Dumas proved was that the atom of oxygen occupies half the volume of the atom of mercury, and twice that of the atom of phosphorus, accepting the atomic weight data of Berzelius.

Weight of equal volumes.	Atomic weight according to Berzelius.	Number of atoms in equal volumes.
O_2 32	16	2
H_2 2	1	2
Hg 200	200	1
P_4 124	31	4
As_4 300	75	4
S_6 ? 192 ?	32	6?

If it be decided to adhere to the volume theory, it is therefore necessary to halve the atomic weight of mercury and to double the atomic weight of phosphorus. Further, in the cases of arsenic and sulphur, the anomalies observed made it necessary to double the atomic weight of arsenic and to treble that of sulphur.

This proved to be a *reductio ad absurdum* of Berzelius' system. Berzelius was confronted with the dilemma that he must either give up the chemical analogies on which he arrived at the atomic weights of mercury, phosphorus, arsenic and sulphur, and change these atomic weights, or give up the volume theory.

Berzelius would do neither the one thing nor the other. He adhered to his atomic weights, and limited the volume theory to certain cases, namely, oxygen, hydrogen, nitrogen, chlorine, bromine, and iodine. As to the theory in general, he says, "in the vapours of simple substances, the ratio between the volume and the number of atoms is subject to variations, which, however, appear to be multiples or submultiples of the number of atoms contained in an equal volume of the permanent or coercible gas of [some] one element."[1]

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[1] Dans les vapeurs des corps simples, le rapport entre le volume et le nombre des atomes est sujet à des variations, qui cependant paraissent être des multiples ou des sous-multiples du nombre d'atomes contenu dans un égal volume d'un gas permanent ou coercible d'un corps simple. Essai, 1835, p. 29.

Even in this limited form, Gmelin did not accept the volume theory. His principle was:—"Let it be granted that heterogeneous substances combine in the simplest possible numerical proportions." (Principle 5.) For water Berzelius had given the formula H_2O, Gmelin gave HO.

The atomic weights arrived at on the basis of the volume theory had yet another defect. Berzelius found that certain atoms, hydrogen, for instance, entered into combination by twos, or multiples of two, and never one at a time. This arose in the following way. In Berzelius's system all strong bases received the formula RO. The amount of hydrochloric acid which combines with this amount of base is composed of two atoms of hydrogen and two atoms of chlorine.

Thus: $RO + H_2Cl_2 = RCl_2 + H_2O$.

This amount of acid, again, combines with an amount of ammonia which contains two atoms of nitrogen. Altogether, Berzelius arrived at the conclusion that the following elements each enter into combination two atoms at a time:—hydrogen, chlorine, fluorine, bromine, iodine, nitrogen, phosphorus, arsenic, and antimony. Accordingly, in each of these cases, two of the atoms of the volume theory act chemically as one atom. So that here was a chemical atom made up of two physical atoms, another *reductio ad absurdum* of the volume theory.

In opposition to all this, Gmelin maintained that "the existence of such small atoms was improbable and their adoption superfluous and troublesome." For the sake of convenience, Berzelius had introduced the use of a special symbol for the double atoms. For instance, two atoms of hydrogen he denoted by H̶, of nitrogen by N̶. These symbols served only to draw attention and to give point to Gmelin's objection. The double atoms of Berzelius were, virtually, the atoms of Gmelin. Use being made of the barred symbols, there was next to no difference between the formulæ of the two systems. Water was H̶O and HO, sulphuretted hydrogen was H̶S and HS.

Berzelius, originally an exponent of Dalton's atom, had introduced a conception of his own, quite subversive of Dalton's. This was the idea of a chemical atom divisible into two physical atoms. It was with special reference to this that Gmelin laid down the principle, "Let no atomic weights be admitted smaller than those which actually occur in combinations." (Principle 6.) This, a mere platitude but for the teaching of Berzelius, was actually a timely, weighty reminder of an axiom of Dalton's theory. Gmelin's principle implied adherence to Dalton's atom in its integrity.

In order to explain why Berzelius' system was supplanted by Gmelin's, there is therefore no need to suppose, with Ladenburg, that the atomic theory had been "abandoned and discredited by the majority of chemists." The only important difference between the two leaders arose from the volume theory. Plausible at first sight, the longer this theory was looked at, the more suspicious it became. Berzelius had to fritter away the theory in more ways than one. Limiting it at first to the elements, he had to limit it still further, under the pressure of Dumas' facts, to a small number of the elements. Again, though as a matter of course he had begun with the assumption that the physical atom and the chemical atom were identical, Berzelius found himself constrained to assume the existence of an atom which was indivisible chemically and physically divisible. Even the authority of Berzelius was inadequate to recommend a system that had become a welter of conflicting ideas and principles. No wonder that his system fell into disrepute, and that Gmelin's came more and more into vogue.[1]

The characteristic feature of the period of chemistry during which the systems of Berzelius and Gmelin were in vogue is the study of the composition of matter by weight. It is a significant fact that during all that time chemists simply failed in their attempts to get Gay-Lussac's law and the current theory of chemistry to elucidate one another. Dalton could find no place for the law in his atomic theory. In 1812, Berzelius wrote to Dalton, expostulating with him for his refusal to accept Gay-Lussac's law. ". . . There are parts of [the atomic] theory, much as science owes to you at present, which demand a little alteration. That part, for example, which obliges you to declare as inaccurate the experiments of Gay-Lussac, on the volumes of the gases which combine. I should have thought rather that these experiments were the finest proof of the probability of the atomic theory."[1] Surely the systems of Gmelin and Berzelius are a proof of how sound were the instincts of Dalton as a theorist. It was the volume theory, Berzelius' interpretation of Gay-Lussac's law, that brought his system to wreck.

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[1] About this time, the chemical doctrines generally of Berzelius fell into disrepute. Here, only the direct causes of the downfall of his atomic weight system have been mentioned.

Likewise accepting Gay-Lussac's law, Gmelin was quite at a loss to arrive at a theory of the composition of matter by volume. Of his six atomic weight principles, not one refers to composition by volume. All that he does is to tabulate the number of atoms of a substance, simple or compound, contained in a given volume. I give a few instances:—

Modern formulæ of substances, and weights of equal volumes.		Formulæ and atomic weights, according to Gmelin.		No. of atoms in equal vols.
O_2	32	O	8	4
P_4	124	P	31	4
H_2	2	H	1	2
Hg	200	Hg	100	2
S_6?	192?	S	16	12?
H_2O	18	HO	9	2
SO_2	64	SO_2	32	2
CO	28	CO	14	2
HCl	36·5	HCl	36·5	1
NH_3	17	NH_3	17	1
PH_3	34	PH_3	34	1

Dalton did not design his theory so as to interpret the composition of matter by volume. His theory was meant as an interpretation of the laws of chemical combination by weight. Berzelius and Gmelin might accept Gay-Lussac's law, but they quite failed to make it the basis of a permanent advance or improvement on Dalton's theory. They left the theory as they found it, essentially a gravimetric theory of matter.

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[1] Henry, pp. 100-1.

CHAPTER XII.

THE CHEMICAL SYSTEM OF GERHARDT AND LAURENT.

Our champions and teachers have lived in stormy times; influences have obstructed a careful consolidation of their judgments.—NEWMAN.

Two methods may be taken in the study of the different systems of chemistry. The first method is fulfilled by a comparison between the atomic-weight data, and between the formulæ of the old and the current systems. The second method, regarding the first as merely preliminary, devotes attention to other considerations; here it is of importance to ascertain principles, and to investigate how far old principles are consistent with one another, and with the principles of to-day.

Of the consequences of attending to coincidences of formulæ and figures, and of ignoring principles, an example is to be found in the account, in Ernst von Meyer's "History of Chemistry," of the changes suggested by Dumas in the atomic weights of Berzelius. The vapour densities of mercury, phosphorus, sulphur, and arsenic having been determined, the atomic weights of these elements were calculated by applying the volume theory of Berzelius. As it turned out, these atomic weights were different from those arrived at on other grounds, by Berzelius himself.

Atomic Weights, O = 16.

	Arrived at by Berzelius.	Arrived at on the Volume Theory.
Hg	200	100
P	31	62
As	75	150
S	32	96

Hereupon, by way of criticism, von Meyer remarks, "A comparison of the atomic weights of Berzelius and Dumas with those of to-day shows us how fully justified the former was in adhering to his own, which he had arrived at after the most mature consideration; Berzelius' values have proved to be the right ones."[1]

Yet von Meyer does not leave principles altogether out of account. Assuming that Dumas was hopelessly in the wrong because his data are wrong, and Berzelius right because his data are right, von Meyer goes on to condemn the want of principle exhibited by Dumas. "In making the above alterations, Dumas' procedure was quite without method"—actually he had made use of the volume theory of Berzelius—"and only helped to complicate matters further"—he compelled Berzelius to set strict limits to the volume theory. "He drew a theoretical distinction between smallest physical and chemical particles"—as it happens, so did Berzelius, whose distinction is forgotten, while that of Dumas remains. "There is justification for the reproach brought against him by many, and more especially by Berzelius, of having introduced obscurity and disorder into the atomic weight system of the latter"—no wonder Berzelius reproached him, he had ruined the credit of Berzelius' volume theory.

Berzelius' data being those accepted now, it has never occurred to the historian that Berzelius' principles are *not* those accepted now, and *are* open to criticism. The principle of the historian seems to be, get modern data by all means, by hook or by crook, but get modern data. As will presently be seen, the fruits of indiscriminate attention to figures, and of neglect of principles are inconsistency, "obscurity," "disorder," and "confusion" in the "History of Chemistry."

Further on, von Meyer says of Dumas, "The whole individuality of the man comes out in his 'Leçons sur la Philosophie Chimique,' . . . in which he treats the development of chemical theories with great clearness. . ." This is at page 274. At page 227, while still discussing the profligacy of Dumas in proposing to alter Berzelius' data on Berzelius' own principles, von Meyer gives a very different impression of Dumas. "For the sake of an unproven hypothesis"—Berzelius' volume theory—"Dumas neglected the most striking chemical analogies (*e.g.*, that between ammonia and phosphoretted hydrogen), and frequently confused things which were perfectly clear." It so happens that Dumas' proposals which von Meyer finds so confusing, are fully discussed in the "Leçons sur la Philosophie Chimique," the whole discussion being a masterpiece of lucidity. What is more, far from "neglecting the analogy between ammonia and phosphoretted hydrogen," Dumas insists upon it. "In ammonia there are three volumes of hydrogen to one of nitrogen. Phosphoretted hydrogen resembles it greatly. Here are two compounds, corresponding to one another, of two elementary substances whose chemical properties have a very great analogy, etc." Either this analogy, Dumas points out, must be given up, or else Berzelius' volume theory; ". . . one must either abjure the fairest analogies of chemical science, . . . or own that in equal volumes phosphorus . . . and nitrogen do not contain the same number of atoms."[1]

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[1] Von Meyer, p. 226.

On the one hand, given the different formulæ that have been used in the case of water only, a careful account of all that these implied to those who used them would go far to be an epitome of the development of scientific chemistry. On the other hand, what can be less instructive and more unscientific than von Meyer's superficial comparison of formulæ and figures? The one formula H_2O, represents the views about water of both Avogadro and Berzelius. Yet how inadequate is the representation! Regarding the nature of hydrogen and oxygen, and of the way in which they combine to form water, Avogadro's views are very much those of to-day. As to Berzelius, when he arrived at the formula H_2O, his views were not very different from those of Dalton, who gave the formula HO.

Divers, in the B.A. address, as I have already pointed out, makes much of "purely chemical" methods, and maintains that chemical change is double decomposition essentially. He says the theory of chemical molecules was brought to light chiefly "through the brilliant work of Gerhardt, Williamson, Laurent, Odling, Wurtz, and others in the purely chemical field." Among these chemists, Gerhardt was the leader. "In the great reformation wrought by the chemists, to whom I have referred, but by Gerhardt in particular, the new light set up in chemistry was the notion of what came to be called 'double decomposition' in chemical change."[1]

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[1] Dans l' ammoniaque on trouve 3 volumes d' hydrogène pour 1 volume d' azote. Or, l' hydrogène phosphoré lui ressemble beaucoup. Ce sont deux composés correspondans de deux corps simples dont les propriétés chimiques présentent la plus grande analogie; . . . il faut ou renoncer aux plus belles analogies de la chimie, ou convenir qu'à volume égal le phosphore . . . et l'azote ne contiennent pas le même nombre d' atomes. Leçons sur la Philosophie Chimique, 1836, pp. 266-7.

In this section, I shall first of all state the general principle of Gerhardt and Laurent, and next exhibit their system in some detail, comparing it with the system of Berzelius. Finally, I shall consider the use of purely chemical methods by Laurent and by Gerhardt.

In the history of chemistry, the association of Gerhardt and Laurent is unique. The beginner of the movement was Gerhardt, who explained his ideas in papers in the "Journal f. pr. Chemie," 1842-3 (27 439, 28 34 and 65, 30 1), and in the "Annales de Chimie et de Physique," 1843 (7 129, 8 238). Eagerly adopting and pursuing these ideas, Laurent made contributions of great value to the movement. The two men became like comrades in arms. Harmony between them was insured by a mutual give-and-take in ideas. Devoted to the same principles, defending one another when attacked, the two chemists worked out their ideas, sometimes singly, sometimes in partnership. Their mature convictions were embodied, Gerhardt's in the "Traité de Chimie Organique" (1853-6), Laurent's in the "Méthode de la Chimie," a posthumous publication translated into English by Odling in 1855.

From the point of view of Avogadro's hypothesis, Gerhardt proposed that the molecules of all substances in the state of gas should be made such as to occupy the same volume. He pointed out that the molecules of many organic substances in the state of gas, acetic acid, for instance, occupied four volumes, while the molecules of water, carbon dioxide, ammonia, sulphur dioxide and oxalic acid occupied two volumes. It was in the region of organic chemistry that Gerhardt was specially successful. Taking the formulæ of

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[1] Divers, pp. 8, 10.

Gmelin, he showed that, if water was evolved in the reactions of organic chemistry, or carbon dioxide, the amount was never one molecule, but always two molecules or multiples of two. Thus, on decomposition one molecule of acetic acid gave marsh gas and two molecules of carbon dioxide. His conclusion was that the molecule of acetic acid was too large, or that of carbon dioxide too small.

Gerhardt and Laurent mention Ampère, but not Avogadro. They do not seem to have known that Avogadro had the advantage in having adopted the hypothesis three years before Ampère, in the more extensive use which he made of it, and in the simplicity of the deductions which he made from it. Anyhow, the great advance made by Gerhardt and Laurent was the adoption of Avogadro's hypothesis.

As regards the elements, there gradually came into fairly wide use, in consequence of Gerhardt and Laurent's teaching, for hydrogen, oxygen, nitrogen, etc., the symbols H_2, O_2, N_2, etc. Gerhardt and Laurent even supposed that the mercury molecule was Hg_2, so that, the molecular weight of mercury being 200 ($H_2 = 2$, $O_2 = 32$), the atomic weight of mercury was 100.

Before proceeding to show the effect of all this on the atomic weight data, I must make a preliminary remark. In a comparison of the atomic weight data of different systems, hydrogen and oxygen are of the first importance. Is water HO, or H_2O? Taking $H = 1$, then, if water is HO, $O = 8$, and the molecular weight of water is 9; if H_2O, then $O = 16$, and the molecular weight of water is 18. However, to have the molecular weight of water changing is a quite unnecessary complication. *The atomic weight of oxygen being fixed at* 16, *the molecular weight of water is* 18, *and for* HO, $H = 2$, for H_2O, $H = 1$. *For the remainder of this chapter it will be assumed that the atomic weight of oxygen remains* 16.

As regards the classification of the metals and their atomic weights relative to oxygen, the system of Berzelius and that of Gmelin were the same. Gerhardt and Laurent, adopting the same classification, halved the atomic weight of mercury, and, accordingly, of all the other metals. Thus, mercuric oxide was no longer HgO, but Hg_2O, and generally RO became R_2O, R_2O became R_4O, R_2O_3 became R_4O_3, etc.

As to the non-metals, the atomic weights of carbon and sulphur (and selenium and tellurium) were the same in all the systems. For other non-metals, Berzelius' data were half those of Gmelin. Here, chiefly by reason of their use of Avogadro's hypothesis, Gerhardt and Laurent were at variance with Gmelin, and in accordance with Berzelius. The following table shows some of these differences and agreements:—

$O = 16$, $S = 32$, $C = 12$.

	Berzelius, 1826.	Gmelin.	Gerhardt and Laurent.
Hg	200	200	100
Na	46	46	23
H	1	2	1
Cl	35·5	71	35·5
N	14	28	14

These atomic weights involve differences in formulæ and also in molecular weights. For water, Gmelin's formula was HO, of the others H_2O.

Modern formulæ.	Berzelius, 1826.	Gmelin.	Gerhardt and Laurent.
H_2O	H_2O	HO	H_2O
HCl	$HCl = 36·5$	$HCl = 73$	$HCl = 36·5$
NH_3	$NH_3 = 17$	$NH_3 = 34$	$NH_3 = 17$
CH_4	CH_4	CH_2	CH_4
H_2S	H_2S	HS	H_2S
Na_2O	NaO	NaO	Na_2O
HgO	HgO	HgO	Hg_2O
$HgCl_2$	$HgCl_2 = 271$	$HgCl = 271$	$HgCl = 135·5$

In accounts of Gerhardt and Laurent's system, attention is often concentrated to excess on the changes they made in atomic weights—quite the less important aspect of their work. In the "Traité," Gerhardt sacrificed his own preferences, and used the atomic weights of Gmelin. Now compromise means that a man may sacrifice much and all except the fundamental thing. So that for Gerhardt there were things of more importance than atomic weights. The truth is that Gerhardt and Laurent were far less concerned about atoms than molecules. For them the important thing in chemistry was the molecule, and the atom of the element had become a subordinate idea, not at all the same thing as the old atom.

There is no historical continuity between Gerhardt and Laurent's system and Berzelius' system, any more than there is between theirs and Gmelin's. Gerhardt and Laurent had reached a theory of the composition of matter by volume, which, unlike Berzelius' volume theory, referred to compounds as well as to elements.

The adoption of Avogadro's hypothesis by Gerhardt and Laurent, involved a great departure from the old ideas. In the case of the elements there is a superficial resemblance between Gerhardt and Laurent's molecule and Berzelius' double atom. That they are different things may be seen in the instances of oxygen and hydrogen. In the case of oxygen, there being no double atom, the comparison with Gerhardt and Laurent's molecule breaks down. Any comparison that is drawn must lie between Berzelius' atom and Gerhardt and Laurent's atom. The two are as different as Dalton's atom and the modern atom. Berzelius' atom is an independent conception, while Gerhardt and Laurent's atom is a subordinate conception, the atom being regarded as a fraction of the molecule. Again, Gerhardt and Laurent's molecule of hydrogen on combination is divided into two atoms, exactly what does not happen to Berzelius' double atom made up of two physical atoms.

Ladenburg completely ignores the breach between Berzelius and Gerhardt, remarking that their agreement as to the atomic weights of the non-metals "must appear striking and peculiar to any unprejudiced person." He goes on—"It is also noteworthy that Gerhardt does not mention Berzelius, and is obviously quite unaware that he, to a large extent, adopts his numbers." However, Gerhardt is not the only great chemist whom Ladenburg has caught nodding. "The Swedish chemist does not appear to have noticed this agreement, since he violently attacks Gerhardt's paper."[1]

One is not bound to accept Ladenburg's naïve suggestion, that Gerhardt and Berzelius each failed to see what nobody could help seeing. I suggest that the inattention of Gerhardt and Berzelius to what Ladenburg thinks so important, coincidences of figures, arose from indifference to these things in view of vital differences in regard to principles.

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[1] Ladenburg, p. 188.

As will instantly be shown, there is no justification whatever for supposing that Gerhardt's criticisms were directed exclusively at the system of Gmelin. Gerhardt and Laurent's proposal to halve the molecules of many compounds, acetic acid, for instance, was directed at Berzelius' system as much as at Gmelin's. Moreover, it is connected with the change from the general formula RO of Berzelius and Gmelin for basic metallic oxides to R_2O, and the simultaneous halving of the atomic weights of the metals. The molecule of acetic acid was determined as the amount that combined to form a neutral salt with one molecule of a base. But nearly all bases, in Gmelin's and Berzelius' systems alike, received the general formula RO, so that in either system the molecule of acetic acid was twice what we now suppose it to be.

To show that Gerhardt's criticisms were not directed at Gmelin's system exclusively, I give the equations for the decomposition of acetic acid according to Gmelin's and Berzelius' formulæ, and according to formulæ used temporarily by Gerhardt, in 1843:—

1. Gmelin—H = 2. C = 12. O = 16.

$$C_4H_4O_4 = 2\ CH_2 + 2\ CO_2.$$

2. Berzelius—H = 1. C = 12. O = 16.

$$C_4H_8O_4 = 2\ CH_4 + 2\ CO_2.$$

3. Gerhardt—H = 1. C = 6. O = 16.[1]

$$C_8H_8O_4 = C_4H_8 + C_4O_4.$$

Gerhardt's intention was to direct attention to an inconsistency in chemical formulæ. He thought it inconsistent that in organic reactions carbon dioxide should be evolved, not one molecule at a time, but two. This criticism touches the system of Gmelin and of Berzelius alike. Gerhardt's argument related to molecules and not to atoms. As inspection of the above equations shows, the argument does not depend upon the use of his own atomic weights, or Gmelin's, or Berzelius'.

It would be an incomplete and misleading account of Gerhardt and Laurent's ideas to say that they based their system on Avogadro's hypothesis exclusively. There is some reason to think that they regarded Avogadro's hypothesis as a short cut, and little more, to conclusions that could be reached with equal certainty by the "strictly chemical" methods.

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[1] Ann. Chim. Phy., 1843, 7, 130.

As to "strictly chemical" methods, here I am only resuming the discussion begun in Chapter VII. of this essay. It was proved there, that the "purely chemical" methods for determining the formula of water really consist in the consideration of a selected reaction. This reaction does lead to the same result as Avogadro's hypothesis, other reactions which tell a different tale being ignored. Further, it was pointed out that the selected reaction which is interpreted in the simplest possible way, is not really so simple as the argument of the "purely chemical" method supposes.

For Gerhardt and Laurent's system, water was extremely important. Water was the chief "type" of the system. The constitution of the oxides and hydroxides of the metals, of the alcohols and aldehydes, the acids and acid anhydrides, of salts and ethers, etc., was understood by reference to the type water. The classification of the system turns on water, so that the "purely chemical" proof of the formula of water being weak, the logical basis of the system is Avogadro's hypothesis after all. Nevertheless, I shall consider Laurent's views on the "strictly chemical" methods first, and then Gerhardt's, to which such prominence has been given by Divers.

The adoption of Avogadro's hypothesis was accompanied by important innovations as to the chemistry of acids and bases. The hypothesis led to the recognition of the distinction between monobasic and dibasic acids. Hydrochloric acid was a monobasic acid, carbon dioxide the anhydride of a dibasic acid. Simultaneously, Gerhardt and Laurent adopted the general formulæ R_2O and ROH for metallic oxides and hydroxides respectively, and in so doing they gained more than one end.

In the first place, the doctrine of types was involved; the new formulæ meant that water was the type of metallic oxides and hydroxides.

In the second place, the formula Hg_2O for mercuric oxide implies that the mercury molecule is Hg_2, like O_2, H_2, etc.

In the third place, the new formulæ fall in with the distinction between monobasic and dibasic acids. Thus the equations in Gmelin's system (HO = 18)

$$ROOH + HCl = RCl + 2HO. \qquad (HCl = 73).$$

$$ROOH + HCO_3 = RCO_3 + 2HO. \qquad (HCO_3 = 62).$$

become respectively, the value of R being halved,

$$ROH + HCl = RCl + H_2O. \qquad (HCl = 36{\cdot}5).$$

$$2ROH + H_2CO_3 = R_2CO_3 + 2H_2O. \qquad (H_2CO_3 = 62).$$

Evidently the recognition of metallic hydroxides as being ROH, and the recognition of the distinction between monobasic and dibasic acids, are bound up together.

Laurent said that the distinction was independent of Avogadro's hypothesis. No sooner had the distinction been unmistakably indicated by the hypothesis, than he was able to see that it might easily have been established without the hypothesis. He mentions carbonic acid particularly. "The carbonates are or are not dibasic, independently of all ideas that we may form regarding equivalents, volumes, or atoms. But we shall see at once that measurement by volume has led us to a right conclusion, and that the carbonates have all the characters of dibasic salts."[1]

Before certain considerations of detail are taken up, there is a consideration that goes to the root of the matter. An acid implies a base. The recognition of the distinction between monobasic and dibasic acids is bound up with the recognition of metallic hydroxides as ROH. There is the objection on the one hand that the use of "purely chemical" methods did not prevent Laurent from giving similar formulæ to potassium and calcium hydroxides. On the other hand, if Laurent had adopted the general formulæ RO and ROOH in place of R_2O and ROH, the necessity for the distinction between monobasic and dibasic acids, but for Avogadro's hypothesis, would not have arisen.

In the "Chemical Method," Laurent laid down no less than sixteen criteria by which to know monobasic and dibasic acids. I give a few of these:—

Monabasic acids yield	Dibasic acids yield
No acid salts.	Acid salts.
No double salts.	Double salts.
One ether.	Two ethers.

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[1] Les carbonates sont ou ne sont pas bibasiques, indépendamment de toutes les idées que nous pouvons nous former sur les équivalents, les volumes ou les atomes. Or nous verrons tout à l'heure que la mesure des volumes nous a conduit à une conséquence juste, et que les carbonates possèdent tous les caractères des sels bibasiques. Ann. Chim. Phy., 1846, 18, 288.

Laurent was aware of exceptions to these rules. He knew that acetic and hydrofluoric acids yield acid salts, and that the tendency to the formation of double salts is well-marked in hydrocyanic and hydriodic acids. Thus the existence of hydrogen potassium fluoride should have led Laurent to regard hydrofluoric acid as H_2F_2, of potassium mercuric iodide to regard hydriodic acid as H_2I_2, of potassium silver cyanide, to regard hydrocyanic acid as $H_2C_2N_2$. Also, the existence of potassium tetroxalate should have led Laurent to formulate oxalic acid as $H_4C_4O_8$. Inasmuch as in all these cases Laurent adhered to the formulæ HF, HI, HCN, $H_2C_2O_4$, one may suspect that he did not pay much heed to evidence that was at variance with the consequences of Avogadro's hypothesis.[1]

Finally, I have to consider Gerhardt's belief in "purely chemical" reactions. His particular conviction is, that chemical reactions are essentially double decompositions. The term he defines thus:—"The chemical reactions . . . in which two substances, by reciprocal decomposition, produce two other substances, are known by the name of *double decompositions*."[2] As to their importance, he says, "This kind of reaction is by far the most frequent in chemistry."[3] Moreover, Gerhardt makes out that many reactions are double decompositions, in spite of appearances to the contrary.

In the B.A. address, Divers' main contention is a revival of Gerhardt's conviction. In Chapter VII. of this essay, I have pointed out that chemical reactions generally are now supposed to be uni- or poly- molecular, not bimolecular as the dogma of double decomposition demands.

Resuming the discussion here, I would point out that the section of Gerhardt's "Traité" in which certain reactions against all appearances are explained as double decompositions is really, as it seems now, an arsenal of instances against his doctrine.

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[1] To nitric oxide Laurent did give the formula N_2O_2, as a conclusion of the "purely chemical" method. (v. Chemical Method, p. 83).

[2] "Les réactions chimiques . . . où deux corps, par leur décomposition réciproque, produisent deux autres corps, sont connus sous le nom de *doubles décompositions*." Traité, 4, 567.

[3] "Cette forme des réactions est de beaucoup la plus fréquente en chimie." Traité, 4, 570.

Gerhardt gives the reaction:—

$$C_6H_6 + Cl_6 = C_6H_6Cl_6.$$

Remarking that the new substance can yield three molecules of hydrochloric acid, he says:—"Thus it is evident that two substances may effect between them a double decomposition, even when but one product is got containing the sum of the elements introduced on either side; only then the products of the double decomposition, instead of separating, remain combined."[1]

It is at the same time perfectly obvious, that addition reactions as such, are *not* double decompositions. A special case of addition is the formation of a polymer, and here again, there is no double decomposition.

Lastly, I may recall Divers' attitude, already scrutinised in Chapter VI. of this essay, as to the molecule of the metals. "It seems impossible from the chemical point of view, to admit that the chemical molecule of sodium and mercury is not bipartite like that of hydrogen and oxygen." Gerhardt and Laurent's views about the molecules of the metals were much the same as Divers'. They thought that the molecules of sodium, mercury, and zinc were "bipartite."

For certain reactions in which mercury and zinc play a part, Gerhardt gives equations which make out that the reactions are double decompositions. One reaction is the decomposition of mercuric cyanide by heat. The equations are:—

$$2HgCN = C_2N_2 + Hg_2. \qquad (Hg = 100).$$

The other reaction is that between hydrochloric acid and zinc. The reaction taking place in two stages, there are two equations:—

$$Zn_2 + HCl = ZnH + ZnCl. \qquad (Zn = 37{\cdot}5).$$
$$ZnH + HCl = ZnCl + H_2.$$

It is apparently to these and suchlike equations that Divers commits himself.

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[1] "On voit ainsi que deux corps peuvent opérer dans leur sein une double décomposition, lors même qu'on n'obtient pas qu'un seul produit, renfermant la somme des éléments mis en présence de part et d'autre; seulement alors les produits de la double décomposition, au lieu de se séparer, restent unis." Traité, 4, 574.

CHAPTER XIII.

THE CHEMICAL SYSTEM OF CANNIZZARO.

The strength of any party lies in its being true to its theory. Consistency is the life of a movement.—NEWMAN.

In order to understand the reform in chemistry of which Cannizzaro was the author, it is necessary to arrive first at some conception of the state of things in 1858, the year of Cannizzaro's suggestions. Chemistry was then in extreme confusion. There were three important systems in use, and, in addition, modifications of these, and compromises between them.

Inorganic chemistry was confused. About the classification of the metals there had been agreement for a time. The influence of Berzelius was powerful here; he had classified the oxides, and put the oxides in series with formulæ to correspond.[1] Gmelin and Gerhardt and Laurent all accepted this classification. In assigning the general formula RO to the chief metallic oxides, Berzelius was followed by Gmelin, but Gerhardt and Laurent took their own way, in giving the formula R_2O. As if this difference were not enough, Regnault proposed a departure from the classification of Berzelius; he assigned the formula RO to some metallic oxides, and to others R_2O. This he did on the basis of his specific heat work, accepting Dulong and Petit's law.[2] It becomes necessary, therefore, to consider the standing of this law in the systems of Berzelius, Gmelin, and Gerhardt and Laurent.

Dulong and Petit's forecast of 1819, that the atomic heats of the different elements are equal, was accepted by chemists with much reserve. In 1826, exceptions to the law being known, Berzelius gave only a qualified assent to it. On reinvestigation of the specific heats, some of these exceptions were removed, and others appeared. About 1850, according to Berzelius' system, the chief known exceptions to the law were silver, sodium, potassium, bismuth, carbon, and bromine.

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[1] See chapter x., p. 73.

[2] He supported his proposals also by reference to considerations of isomorphism.

Between 1819 and 1850, the tendency of chemical speculation was not such as to establish Dulong and Petit's law. It is true that in Berzelius' system the exceptions were comparatively few, but Regnault's proposal to make them fewer, by regarding the oxides of sodium, potassium, and silver as R_2O generally, instead of RO, did not meet with wide approval. Besides, Berzelius' system was no longer in the ascendent. Gmelin's system came into vogue, and then Gerhardt and Laurent's. In these systems the exceptions to Dulong and Petit's law are more numerous than in Berzelius'. In Gmelin's system they are:—silver, sodium, potassium, gold, carbon, bromine, iodine, phosphorus, arsenic, and antimony; 6·4 being the atomic heat of most of the elements, that of the exceptions was, in nearly all cases, about 12·8. In Gerhardt and Laurent's system, the exceptions were the same as in Gmelin's, with the addition of sulphur; the bulk of the elements had the atomic heat 3·2, the exceptions 6·4 mostly.

About 1858, if the system of Gerhardt and Laurent was in the ascendent, the systems of Gmelin, Berzelius, and Regnault[1] had yet their adherents.

In organic chemistry the confusion was yet greater. Gerhardt and Laurent's ideas, at first despised, came more and more into vogue. The movement which they began was powerfully supported by the work and the influence of Williamson, Odling, Brodie, Hofmann, Frankland, and Wurtz. Yet in 1854, Gmelin's system was still so widely used that Gerhardt, in order to spread his ideas, expressed them in the "Traité de Chimie Organique" in terms of Gmelin's atomic weights and formulæ.

So many different systems involved a multiplicity of formulæ; for water, at least five were in use—HO, H_2O, $\bar{H}O$, H_2O_2, $\frac{H}{H}O_2$. (The last two formulæ arise in attempts at compromise between Gerhardt and Laurent's ideas, and those of Berzelius, and of Gmelin.) For a substance such as acetic acid as to the constitution of which there were considerable differences of opinion, there were formulæ in bewildering profusion.

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[1] Regnault did not carry out his own suggestions. In the Cours Elémentaire de Chimie, 3rd ed., 1851, for the metals, including silver, potassium and sodium, he gives the same atomic weights as Gmelin.

Besides, the same formula meant different substances to the chemist, according to the school to which he belonged. H_2O_2 might mean water or hydrogen peroxide; C_2H_4, marsh gas or ethylene; $C_4H_4O_4$, acetic acid or fumaric acid; CuCl was cuprous or cupric chloride.[1]

Such in organic and inorganic chemistry was the state of confusion which was dispelled by the suggestions of Cannizzaro. In Tilden's "Short History,"[2] mention is made but once of Cannizzaro, and that is in connection with Dulong and Petit's law. If he did no more than arrive at atomic weights on the basis of Dulong and Petit's law, he was anticipated there by Dulong and Petit. Nevertheless, Cannizzaro's work has other and more important aspects than the one mentioned by Tilden.

His work, roughly speaking, is complementary to Gerhardt and Laurent's; on the basis of Avogadro's hypothesis he systematised inorganic chemistry. Gerhardt and Laurent were far more successful in organic than in inorganic chemistry. What these chemists seem to have neglected, Cannizzaro took up; he studied the data that since the time of Dumas had been accumulating as to the vapour density of inorganic substances. Applying Avogadro's hypothesis, Cannizzaro determined the molecular weights of many inorganic substances.

Like Gerhardt and Laurent, Cannizzaro considered molecules first and atoms afterwards. The meaning of the atom he explains as follows:—"The different amounts of one and the same element contained in different molecules are all of them whole multiples of a certain quantity, which, since it is always found undivided in compounds, is rightly denoted an atom."[3] This is surely a very significant utterance, first, as being a practical definition of the atom, second, because the atom is here defined, with reference to the molecule. In the systems of Berzelius and Gmelin, the atomic weight methods were pretty numerous, and (except for the volume theory, which proved doubtful after all) there was no primary or principal one. Cannizzaro arrives first at the molecular weight of inorganic compounds, and thence at the atomic weights of their constituents. For the first time, the atomic weights of such different elements for example, as sulphur, carbon, iodine, arsenic, tin, mercury, boron, and silicon, were determined from a single point of view.

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[1] Klassiker, 30, 57. [2] p. 75. [3] Klassiker, 30, 10.

As to the classification of metallic compounds, Cannizzaro followed Berzelius, but not completely. The difference arises through Cannizzaro's classifying with mercurous and cuprous chlorides the chlorides of silver, potassium, sodium, and lithium. To these, having satisfied himself that mercuric chloride was $HgCl_2$ and mercurous chloride HgCl, he gave the general formula RCl. To cupric, zinc, lead, calcium, stannous and platinous chlorides, which he classified along with mercuric chloride, he gave the general formula RCl_2. Accordingly, Cannizzaro was able to ascertain the atomic weights of many of the metals.

As a matter of history, Dulong and Petit's law did not recommend itself to chemists, not even to Cannizzaro; his attitude towards the law was not one of mere acquiescence. By applying Avogadro's hypothesis, he had determined the atomic weights of the non-metals and of mercury, zinc, and tin. By classification, he arrived at the atomic weights of other metals. Simultaneously, he tried if these atomic weights fell in with Dulong and Petit's law, and found that they did. Forthwith, Cannizzaro put his trust in Dulong and Petit's law in order to arrive at atomic weights, in cases where no other evidence was available.

Lastly, Cannizzaro instituted a reform with respect to the molecular formulæ of the elements. He regarded the molecule of the element as polyatomic in general—a great advance on all previously accepted teaching about the elements. Gay-Lussac's law, along with Avogadro's hypothesis, leads inevitably to the doctrine that the molecule of the elements is polyatomic. This proved a stumbling block to everybody before Cannizzaro. Dalton simply rejected both hypothesis and law. Dumas had arrived at much the same views as Cannizzaro, but withdrew from his views, in the face of opposition. Gerhardt and Laurent, having arrived at the true molecular weight, 200 for mercury, put a forced construction on this. They maintained that the molecule of the element was in general biatomic. Hence the mercury molecule was Hg_2, and the atomic weight of mercury 100. Cannizzaro accepting the experimental facts, simply interpreted them as usual so as to arrive at the molecular and atomic weights of the elements. Accordingly, he was able to explain data that had been lying unexplained since the day of Dumas. He formulated the oxygen molecule as O_2, that of sulphur as S_6, of phosphorus as P_4, of mercury as Hg.

At a congress of chemists, held at Carlsruhe in 1860, in order to take into consideration, and if possible to remedy, the confusion then reigning in chemistry, Cannizzaro's ideas, first published in 1858, were made widely known. The effect was unique; the old systems, variations and all, melted away. Odling, in 1864, remarked on the unanimity of belief among English chemists as to atomic weights. "After the great . . . antagonism of opinion which has existed for the last dozen years or so, I . . . notice the substantial agreement among English chemists as to the combining proportions of the elementary bodies, and the molecular weights of their . . . compounds. The unanimity is . . . greater than has ever been the case since Dalton published his 'New System of Chemical Philosophy.'"[1]

What was the secret of the readiness of chemists almost everywhere, to follow Cannizzaro's suggestion, and accept the guidance of Avogadro's hypothesis throughout chemistry? Had not Gerhardt and Laurent proposed the same thing, and had not their proposals been received by chemists with much hesitation and even opposition? Gmelin's system was still in wide use in 1854-6, while Gerhardt was publishing the "Traité." Why did chemists stubbornly persist in refusing to accept the guidance of Avogadro's hypothesis in organic chemistry? What advance had Cannizzaro made on Gerhardt and Laurent?

I suggest the following explanation. The movement begun by Gerhardt and Laurent had tended more and more to the cultivation of purely chemical methods. The discoveries that we associate with the names of Williamson and Hofmann, for instance, show this. That Avogadro's hypothesis, or nothing, is the special basis of Gerhardt and Laurent's system, was what they failed to realise. Regarding it as a makeshift at best, they were willing that it should fall into the background: they put their trust in "purely chemical" methods. But the school of Gerhardt and Laurent had no monopoly of "purely chemical" methods. The truth is, that there never has been devised a system of chemistry, professing a knowledge of the relative size and constitution of molecules, and postulating that "purely chemical" evidence is to be ignored. Just as all politicians profess patriotism, the chemists of all schools profess "chemical methods," and if these methods were self-sufficient, the history of chemistry would abound less than it does with systems. In fact, Cannizzaro's suggestions, and even Gerhardt and Laurent's were long set aside by Kolbe, on the ground of adherence to "purely chemical" methods. Japp, in the Kekulé Memorial Lecture, has pointed out that "until 1870 he [Kolbe] continued to use Gmelin's equivalents instead of our present atomic weights." This arose from his "extraordinary power of expressing chemical reactions in terms of chemical constitution," which "was unfortunately coupled with an almost complete inability to realise the force of arguments drawn from physical laws." Nor did Kolbe express contrition for his adherence to the "strictly chemical" methods. He "afterwards contended that his mistaken adherence to the old equivalents had facilitated his discovery of the constitution of acids, aldehydes, and ketones, and his prognosis of secondary and tertiary alcohols."[1]

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[1] C. N., 10, 149.

"Strictly chemical" methods are much more available for organic than for inorganic chemistry. There had therefore been no principle common to both branches of the science, and Dumas even suggested that there were two sciences of chemistry, organic and inorganic.[2] Cannizzaro referred both branches to one principle, and adhered to this principle with complete assurance, which in itself inspired confidence. He showed that Avogadro's hypothesis, with which the organic chemistry of Gerhardt and Laurent was in accordance, was of immense value in inorganic chemistry. Cannizzaro had uttered the right word. The unification of chemistry was possible. Hence the emotion of Lothar Meyer, as his mind grasped Cannizzaro's ideas:—"There fell as it were scales from my eyes, my doubts were dispelled, and in place of them there came a feeling of the calmest confidence."

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[1] J. C. S., 73, 110.

[2] Klassiker, 30, 59.

On the progress of chemistry Cannizzaro's teaching had an immediate and great effect; it led up to the establishment on a sound basis of two great doctrines. The periodic system, in its original form,[1] was based on Cannizzaro's atomic weights. In 1866, Newlands said, "No relation could be worked out of the atomic weights under any other system than that of Cannizzaro."[2] In regard to the doctrine of valency, Frankland says that until Cannizzaro "had placed the atomic weights on their present consistent basis, the satisfactory development of the doctrine was impossible."[3]

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[1] Newlands' Law of Octaves, 1864.

[2] C. N., 13, 113.

[3] Experimental Researches, p. 154.

CHAPTER XIV.

THE RELATIVE STANDING OF DALTON'S ATOMIC THEORY AND AVOGADRO'S HYPOTHESIS.

Truth is the only merit which gives dignity and worth to history.—LORD ACTON.

By way of conclusion, I shall attempt in this chapter to give an estimate of Dalton's services to chemistry, and in particular, to determine the relation between his theory of chemistry and the modern one.

First of all, it is only right to take into consideration the criticism which has already been passed upon Dalton. I wish to direct attention to certain claims which have been made on Dalton's behalf by Roscoe.

Roscoe, in his life of Dalton, makes the following assertion:—"The law of the equal expansion of all gases for equal increments of temperature has been generally known on the Continent as "Gay-Lussac's" or "Charles' law," but ought to be called "Dalton's law of expansion," as he first announced it and gave experimental evidence of its truth, and the claims of the Manchester philosopher are generally now allowed."[1] Anyone, by looking at half-a-dozen modern books on physical chemistry, can see for himself how far Dalton's claims are now allowed. Better, however, to consider the case on its merits.

Regarding the expansion of gases there are really two stages of information. The first consists in the knowledge that all gases expand equally, the second, in a knowledge of the rate at which a gas expands at different temperatures. For the first piece of knowledge, Gay-Lussac in his paper of a few months later than Dalton's, gives the credit to Charles, as having discovered it fifteen years before.[2]

As to the rate of gaseous expansion at different temperatures, the truth is, that Dalton's experimental results are the reverse of what he expected, and that either way he was wrong. This is partly discussed in Balfour Stewart's "Heat." "According to Gay-Lussac, the augmentation which a gas receives when the temperature increases 1° is a certain fixed proportion of its initial volume at 0°C.; while, according to Dalton, a gas at any temperature increases in volume for a rise of 1° by a constant fraction of its volume at that temperature." "The dilatation of gases has since been investigated by Rudberg, Dulong and Petit, Magnus, and Regnault, and the result of their labours leaves little doubt that Gay-Lussac's method of expressing the law is much nearer the truth than Dalton's."[1]

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[1] Roscoe, p. 96.

[2] On this account, the law is ascribed to Charles by Clerk Maxwell. Heat, p. 29.

As reference to the original paper shows, Dalton did indeed expect that a quantity of gas would expand, when raised through equal intervals of temperature, more at a high than at a low temperature. Such was Dalton's anticipation on theoretical grounds. On experiment with air, hydrogen, oxygen, carbon dioxide, and nitric oxide, Dalton found the opposite of what he anticipated. Starting at 55° F. with 1000 parts of air, the expansion between 55° and 132½° was 167, between 132½° and 210° only 158 parts.[2]

Roscoe further makes the following assertions:—(1) Dalton's "great achievement was that he was the first to introduce the idea of quantity into chemistry."[3] (2) "Dalton gave to the world the final and satisfactory proof of the great principle, long surmised and often dwelt upon, that in every kind of chemical change no loss of matter occurs."[4] (3) "Dalton, by determining the relative weights of the atoms which take part in chemical change, proved that every such change . . . can be represented quantitatively by a chemical equation."[5]

Among chemists the prevailing belief is, that the credit of all these achievements is due to Lavoisier. Mallet, in the Stas Memorial Lecture, after referring to the work of van Helmont, Boyle, Boerhave, Black, and Cavendish, in connection with the doctrine of the conservation of matter, says, the doctrine "assumed its due importance, and began to receive universal recognition, with the constant appeal to the balance which Lavoisier made, and taught others to make."[1] So much for the first two assertions of Roscoe. As to the third, I need only give the references to the original papers, in order to establish Lavoisier's claims. An early attempt of Lavoisier's at a chemical equation will be found in a paper of date 1782.[2] He uses a chemical equation in a paper of date 1788.[3] Finally, in the "Traité de Chimie," he says:—"For nothing is created, either in artificial operations or in nature, and, in principle, it may be said that, before and after every operation, there is an equal quantity of matter; that the kind and amount of the elements (les principes) is the same, and that there occur only changes and modifications.

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[1] Balfour Stewart's Heat, 5th ed., 1888, p. 63.

[2] Klassiker, 44, 28-9.

[3] Roscoe, p. 153.

[4] Roscoe, p. 7.

[5] Roscoe, p. 7.

"On this principle is based the whole art of chemical experiment; one is bound to suppose always a real equality or equation between the elements (les principes) of the substance in question, and those which are got from it by analysis. Thus, since must of grapes gives carbon dioxide and alcohol, I can say that *must of grapes = carbon dioxide + alcohol*."[4]

The truth is that eulogy of Dalton is uttered at random, and has been carried to lengths far beyond the requirements of science.

In attempting to check these assertions of Roscoe, I am not, in any way, actuated by a wish to disparage Dalton. My object is to draw attention to the "extreme license of affirmation" about Dalton that prevails among his eulogists. In this way only, light can be thrown on the assertion that "Dalton's theory has stood the test of time," and such like. I have therefore given instances of injustice done to other men of science in what are supposed to be the interests of

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[1] J. C. S., 63, 10. [2] Œuvres de Lavoisier, 2, 509. [3] Œuvres, 2, 777.

[4] . . . car rien ne se crée, ni dans les opérations de l'art, ni dans celles de la nature, et l'on peut poser en principe que, dans toute opération, il y a une égale quantité de matière avant et après l'opération; que la qualité et la quantité des principes est la même, et qu'il n'y a que des changements, des modifications. C'est sur ce principe qu'est fondé tout l'art des expériences en chimie: on est obligé de supposer dans toutes une véritable égalité ou équation entre les principes du corps qu'on examine et ceux qu'on en retire par l'analyse. Ainsi, puisque du moût de raisin donne du gaz acide carbonique et de l'alcool, je puis dire que le *moût de raisin = acide carbonique + alcool*. Œuvres, 1, 101.

Dalton. In the composite man of science, to whom Roscoe gives the name of Dalton, it is easy to discern the features of Charles, Gay-Lussac, and Lavoisier. Plainly, the effect of all this is to obscure the individuality of Dalton, and in his interests, therefore, to justify and make indispensable an impartial enquiry into his merits. Under the circumstances, it is not to be wondered at if the result of such an enquiry should be different from the customary estimate of Dalton.

Dalton's contributions to chemical thinking may conveniently be classified under the heads of law and theory.

The experimental basis of Dalton's system of chemistry is to be found in the three laws of chemical combination by weight. Two of these laws, that of multiple and reciprocal proportion, necessarily involve, and depend upon, the law of constant proportion.

The law of constant proportion was a burning question about the beginning of the nineteenth century. Proust upheld the law against Berthollet. At the present day it is recognised that in the contentions of Berthollet there is much that is right. What we perhaps now are slow to recognise is how much the sound element in Berthollet's doctrine sustained the unsound. It is often now supposed that chemists were satisfied by 1806, certainly by 1808, that Berthollet was wrong and Proust right. Thus Clarke says:—"The memorable controversy between Proust and Berthollet had by this time [1808] exhausted its force, and nearly all chemists were satisfied that the law of definite or constant proportions must be true."[1] On the contrary, I suspect that in 1808, and even later, the currency of Berthollet's views was wider than Clarke thinks. Gay-Lussac in 1808 thought, with Berthollet, that the law of constant proportions held for gases, but, except in special cases, not for liquids and solids.

Gay-Lussac indeed maintains that compounds are formed in variable proportions, unless these proportions are determined by special circumstances. "We must first of all admit, with M. Berthollet, that chemical action is exercised indefinitely in a continuous manner between the molecules of substances, whatever their number and ratio may be, and that in general we can obtain compounds with very variable proportions. But then we must admit at the same time that—apart from insolubility, cohesion, and elasticity, which tend to produce compounds in fixed proportions—chemical action is exerted more powerfully when the elements are in simple ratios or in multiple proportions among themselves, and that compounds are thus produced which separate out more easily."[1]

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[1] Clarke, "The Atomic Theory," Manchester Memoirs, vol. 47 (1903), No. 11, p. 9.

Dalton made a great advance by his method of expressing the composition of matter. The way had been to give the composition of 100 parts. Dalton's way is to give the composition of two compounds of the same elements with regard to a certain amount of one of the elements. This at once brought to light the law of multiple proportions, Dalton's great discovery. Further, the composition of numerous substances being expressed in this way, the law of reciprocal proportions was revealed.

As to the law of constant proportion, such was the bent of Dalton's mind that in all likelihood he never felt a moment's doubt of its truth. In securing recognition of the law, his influence was of much avail. The prosperity of his doctrine of multiple proportion carried with it full recognition of the law of constant proportion.

Dalton's service to chemical theory is, that in reviving the atomic theory, he gave an immense impulse to accurate thinking in terms of atoms and molecules. In terms of atoms he explained chemical and physical phenomena, and in particular, expressed the law of conservation of matter. He said, the weight of a compound atom is equal to the sum of the weights of the constituent atoms.

Dalton's speculations proved a great stimulus to scientific thought. Avogadro was familiar with the exposition of Dalton's ideas in Thomson's "System of Chemistry." In Avogadro's paper of 1811, Dalton is mentioned again and again.[2]

Dalton inaugurated the epoch in chemistry of the gravimetric composition of matter. By the particular form which he impressed on the atomic theory, he accounted for the laws of combination in multiple and reciprocal proportion. Inasmuch as at the same time he rejected Gay-Lussac's law, the conclusion seems inevitable, that Dalton's atomic theory was a gravimetric, and not a volumetric theory of matter. I have already pointed out how unfortunate were Berzelius' attempts to explain the composition of matter by volume. Gmelin's system of chemistry was not influenced by Gay-Lussac's law, and, so far, was true to the original.

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[1] A. C. R., 4, 23-4. [2] See A. C. R., 4, 34.

A fair test of a scientific idea is, does it, on the long run, among the men of science who adopt it, lead to something approaching unanimity, and particularly in regard to quantitative matters?

The real test of any particular form of the atomic theory is, does it lend itself to the measurement of atoms? The idea of atoms was not due to Dalton. What he originated was a persistent attempt to arrive at atomic weights. This was one of the main objects of the New System of Chemical Philosophy. "Now it is one greaf object of this work, to show the importance and advantage of ascertaining *the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle.*"[1]

The truth is, that in the form which Dalton gave to the atomic theory, there never was any certainty about atoms and atomic weights. From the very outset almost, Davy and Wollaston detected this flaw in the theory. Atomic weights were decided according to a set of arbitrary rules, any one of which, moreover, might at any moment be abandoned. In the attempt to determine atomic weights, Dalton failed, on his own confession. "The second object of the atomic theory, namely, that of investigating the *number* of atoms in the respective compounds, appears to me to have been little understood, even by some who have undertaken to expound the principles of the theory. . . . It is necessary not only to consider the combinations of A with B, but also those of A with C, D, E, etc., as well as those of B with C, D, E, etc., before we can have good reason to be satisfied with our determinations as to the *number* of atoms which enter into the various compounds. Elements formed of azote and oxygen appear to contain portions of oxygen, as the numbers 1, 2, 3, 4, 5 successively, so as to make it highly improbable that the combinations can be effected in any other than one of two ways. But in deciding which of these two we ought to adopt, we have to examine not only the compositions and decompositions of the several compounds of these two elements, but also compounds which each of them forms with other bodies. I have spent much time and labour upon these compounds, and upon others of the primary elements, carbon, hydrogen, oxygen, and azote, which appear to me to be of the greatest importance in the atomic system; but it will be seen that I am not satisfied on this head, either by my own labour or that of others, chiefly through the want of an accurate knowledge of combining proportions."[1]

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[1] A. C. R., 2, 29.

If Dalton's misgivings as to the past were justified, his hopes for the future were not. The systems of Berzelius and Gmelin bring the objections of Davy and Wollaston to a head. Dalton's theory, by its very nature, was always being confronted with dilemmas which it could never meet but in an arbitrary way. The systems of Berzelius and Gmelin abound with instances where "it is highly improbable that combination can be effected in any other than one of two ways." Which of these two ways was right, was always more than the theory could tell.

Those who maintain that Dalton's conception of the atom is not outworn, but is still with us, have much to answer for. When Thorpe says that "the characteristic feature of the chemistry of our time is, in a word, the development and elaboration of Dalton's doctrine," it is a palpable omission that Thorpe should not define precisely what he understands by "Dalton's doctrine." There are four great systems of chemistry—Berzelius', Gmelin's, Gerhardt and Laurent's, and Cannizzaro's. If Dalton's atom is indeed "the central, dominant conception" of these four systems, the conception must have been a very futile one; it leads to complete uncertainty about atomic weights.

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[1] New System of Chemical Philosophy, vol. II., part 1, 1827, quoted from Henry, pp. 92-93.

The differences between the four systems are of a remarkable kind. The atom of oxygen being 16, that of hydrogen, according to Gmelin, is 2, and according to Cannizzaro 1. Hence Gmelin might say that Cannizzaro had split the atom of hydrogen. The "characteristic feature" of chemistry up to 1860 is, one may say, that chemists were continually splitting one another's atoms.

As to the modern system, it differs from Dalton's in being concerned with the composition of matter by volume, and with this in the first place. Gay-Lussac's law and Avogadro's hypothesis are the foundation of chemical theory.

Not content with the fact that Dalton discovered the law of combination in multiple proportions, that he gave a great impulse to the chemical theory of the nineteenth century, and that his conception of the atom dominated nearly fifty years of chemical work, Dalton's eulogists must needs insist that his ideas are still adhered to, in a system of chemistry dominated by a hypothesis to which Dalton was opposed.

Attention must therefore be directed to another instance of Roscoe's loose assertions to the supposed credit of Dalton. "He first explained the *facts* of chemical combination by a *theory* which has stood the test of time, and is not contradicted by any known phenomenon of chemical action."[1]

As to Dalton's having "first explained the facts of chemical combination," the truth is, that he explained only part of the facts. Not believing in Gay Lussac's law, Dalton did not seek to explain it, unless in the sense of explaining it away.

As to Dalton's theory having "stood the test of time," I can only repeat what has been said in this essay already, that Dalton's theory is incompatible with Avogadro's hypothesis, and that Avogadro's hypothesis is the basis of the current theory of chemistry.

Again, Dalton's theory and the modern one differ in their ways of expressing the gravimetric composition of matter. When two substances have the same element in common, there are three ways of expressing their composition. The first way is that of percentage composition. The second way is Dalton's, by reference to a certain amount of the element in question. The third and modern way, on which much emphasis was put by Cannizzaro, is by reference to the molecular weights of the substances. Dalton's way is a great advance on the first, and Cannizzaro's is as great an advance on Dalton's.

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[1] Roscoe, p. 129.

If, the further from Dalton, the nearer to his teaching, then Cannizzaro's atom, the modern atom, may be the Daltonian atom. This is the belief of Ostwald, and presumably of Thorpe. Divers can only maintain that "Dalton's atom is the modern molecule *confused* with the idea of the atom." The other view is just as tenable, that his atom is the modern atom, *confused* with the idea of the molecule. Neither of these views, surely, is the "best possible construction" that can be put on the Daltonian atom. In the place of these unfortunate attempts to confuse it with this and that conception of modern chemistry, I have suggested in Chapter IX. of this essay that Dalton's atom, incompatible, as Dalton saw, with Avogadro's hypothesis, was a unique conception, which reigned supreme during the epoch of gravimetric chemistry, and which was, from its very nature, abandoned when Avogadro's hypothesis was adopted.

The atom, in the modern theory of chemistry, is a "dependency of the molecule." This doctrine I have illustrated in the first part of this essay, and Divers maintains it for his special theory "divested of all reference to the physical constitution of matter." The old order is to consider atoms first and then molecules (compound atoms). The Daltonian method is to arrive straightway at atomic weights on the basis of the laws of multiple and reciprocal proportions. The new order is to consider molecules, and then analyse molecules into atoms. "By the death of Hermann Kopp," says Thorpe, "the army of science lost one of its generals of division." Kopp in 1873, in Wöhler's "Grundriss der Unorganischen Chemie," pp. 350-1, and indeed, so early as 1863, in his "Theoretische Chemie," pp. 354-7,[1] adopted the order, molecules before atoms, molecular weights before atomic weights. Accordingly, the consideration, in a chemical text-book of the present day, of atoms before molecules is nothing but a survival from a chemical system long out of date.

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[1] These references, in proof of the strategy of Kopp, I owe to Professor Japp.

Avogadro's hypothesis being the fundamental hypothesis of chemistry, other doctrines concerning molecules and atoms are to be subordinated to it. It is for this that Cannizzaro pleads in the Faraday Memorial Lecture. "We must explain and legitimise the different auxiliary criteria (specific heat, isomorphism, chemical analogy) to which we have recourse, . . . by first trying them on the touchstone of the theory of Avogadro and Clausius."[1] The method of many text-books, of constructing a system of chemistry like a piece of patchwork, of giving molecular weight and atomic weight methods, as if they had no coherence with one another, or with the definitions of the molecule and the atom, merely recalls the epoch of Gmelin and Berzelius, whose systems were built up on a cluster of independent and often conflicting principles.

Finally, the modern theory draws a distinction between the molecule and the atom of an element, which is absolutely foreign to the Daltonian theory.

Avogadro himself, it would seem, thought he had made an advance on Dalton's theory, an advance which was yet compatible with the original theory. He says, "There are many points of agreement between our special results and those of Dalton, although we set out from a general principle, and Dalton has only been guided by considerations of detail. This agreement is an argument in favour of our hypothesis, which is at bottom merely Dalton's system furnished with a new means of precision from the connection we have found between it and the general fact established by M. Gay-Lussac."[2]

In writing this, Avogadro had evidently no foreboding of how long his ideas would be despised and rejected by chemists. Actually, not for thirty years, that is, not till the day of Gerhardt and Laurent, did chemistry take the trend of thought which Avogadro suggested. The difference between Dalton's system and Avogadro's was no trifle to the chemists who felt most the influence of Dalton.

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[1] J. C. S., 25, 962. [2] A. C. R., 4, 51.

> "Oh, the little more and how much it is,
> And the little less, and what worlds away."

When, about 1827, Dumas found himself constrained to regard the "atoms" of the elements as divisible, Berzelius was testy with him. "It is absurd to assume fractions of atoms, and it was formerly the custom to abandon hypotheses as soon as they led to absurdity."[1]

Once known, Dalton's idea came straightway into currency in chemistry, and reigned supreme in the system of Berzelius and then of Gmelin, in spite of attempts by Avogadro, by Ampère, by Dumas, and by Prout to introduce the ideas of the molecule and the atom. At length, Gerhardt and Laurent formulated again the distinction between the molecule and the atom; from that time Dalton's atom steadily lost vogue. Accordingly, Ostwald's view, that the modern atomic hypothesis is the atomic theory of Dalton, and Divers', that Dalton's atom is the modern molecule, are equally tenable and equally untenable. Ostwald is simply emphasising the aspect of Dalton's atom that Divers neglects; the aspect of Dalton's atom that Ostwald ignores, Divers emphasises.

Finally, by way of a summary of the argument, I propose to consider Ostwald's views, already given in Chapter VII., that modern chemistry is a product of the molecular hypothesis and the atomic hypothesis, and that the molecular hypothesis "has played a similar, though not so important a part in the development of the science as the atomic hypothesis."

All this involves the assumption that the molecular and atomic hypotheses are conceptions independent of one another —a very questionable assumption. The atom can be defined with reference to the molecule; it is doubtful if any other definition is sufficient. The atomic weights of the non-metals can all be determined by reference to the molecular weights of their compounds; that these atomic weights can be determined with certainty, apart from molecular weights, has yet to be proved.

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[1] Quoted from Ladenburg, p. 104.

On the historical question, Ostwald's view is not justified by the facts of chemical history. On the one hand, apart from Avogadro's hypothesis, chemists never have been able to agree about atomic weights. On the other hand, the recognition of this hypothesis by chemists has always led to great advances in chemistry. In organic chemistry, the advances associated with the school of Gerhardt and Laurent, ostensibly based on "purely chemical" methods, are truly based on the hypothesis. Again, neglect of the hypothesis, coupled with adherence to the atomic hypothesis, led, by 1860, to a state of extreme confusion in chemistry. On the reassertion of Avogadro's hypothesis by Cannizzaro this confusion was dispelled, almost as if by magic. In recent years, the molecular hypothesis has been of the utmost service in physical chemistry. I should not venture to assert the value of Avogadro's hypothesis in the development of physical chemistry, apparently in opposition to Ostwald, were I not able to support my position by a reference to the authority of Nernst. "It continually became clearer to me that, in the theoretical treatment of chemical processes, . . . the most important foundations are" the doctrine of energy and "the rule of Avogadro, which seems to be an almost inexhaustible 'horn of plenty' for the molecular theory."[1]

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[1] Nernst, pp. xii.-xiii.

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